

FILE 'HOME' ENTERED AT 15:10:14 ON 06 MAR 2009

FILE 'REGISTRY' ENTERED AT 15:10:28 ON 06 MAR 2009
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Property values tagged with IC are from the ZIC/VINITI data file provided by InfoChem.

STRUCTURE FILE UPDATES: 4 MAR 2009 HIGHEST RN 1115640-24-8
DICTIONARY FILE UPDATES: 4 MAR 2009 HIGHEST RN 1115640-24-8

New CAS Information Use Policies; enter HELP.USAGETERMS for details.

TSCA INFORMATION NOW CURRENT THROUGH January 9, 2009.

Please note that search-term pricing does apply when conducting SmartSELECT searches.

REGISTRY includes numerically searchable data for experimental and predicted properties as well as tags indicating availability of experimental property data in the original document. For information on property searching in REGISTRY, refer to:

<http://www.cas.org/support/stnqgen/stndoc/properties.html>

=> s 6674-22-2/cn

=> s 6674-22-2/rn
L2 1 6674-22-2/RN

=> file caplus
COST IN U.S. DOLLARS

	SINCE FILE	TOTAL
	ENTRY	SESSION
FULL ESTIMATED COST	7.75	7.97

FILE 'CAPLUS' ENTERED AT 15:13:10 ON 06 MAR 2009
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FILE COVERS 1907 - 6 Mar 2009 VOL 150 ISS 11
FILE LAST UPDATED: 5 Mar 2009 (20090305/ED)

Caplus now includes complete International Patent Classification (IPC) reclassification data for the third quarter of 2008.

CAS Information Use Policies apply and are available at: www.cas.org/casinfo

<http://www.cas.org/legal/infopolicy.html>

This file contains CAS Registry Numbers for easy and accurate substance identification.

=> s L2
L3 3786 L2

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=> file registry
COST IN U.S. DOLLARS          SINCE FILE      TOTAL
                                ENTRY        SESSION
FULL ESTIMATED COST          0.50          8.47

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FILE 'REGISTRY' ENTERED AT 15:13:28 ON 06 MAR 2009
USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.
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Property values tagged with IC are from the ZIC/VINITI data file provided by InfoChem.

STRUCTURE FILE UPDATES: 4 MAR 2009 HIGHEST RN 1115640-24-8
DICTIONARY FILE UPDATES: 4 MAR 2009 HIGHEST RN 1115640-24-8

New CAS Information Use Policies, enter HELP USAGETERMS for details.

TSCA INFORMATION NOW CURRENT THROUGH January 9, 2009.

Please note that search-term pricing does apply when conducting SmartSELECT searches.

REGISTRY includes numerically searchable data for experimental and predicted properties as well as tags indicating availability of experimental property data in the original document. For information on property searching in REGISTRY, refer to:

<http://www.cas.org/support/stnqgen/stndoc/properties.html>

=> s 7320-37-8/rn
L4 1 7320-37-8/RN

=> d L4

L4 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2009 ACS on STN
RN ***7320-37-8*** REGISTRY
ED Entered STN: 16 Nov 1984
CN Oxirane, 2-tetradeacyl- (CA INDEX NAME)
OTHER CA INDEX NAMES:

CN Hexadecane, 1,2-epoxy- (6CI, 7CI, 8CI)
CN Oxirane, tetradecyl- (9CI)
OTHER NAMES:
CN 1,2-Epoxyhexadecane
CN 1,2-Epoxyhexadecene
CN 1,2-Hexadecene epoxide
CN 1,2-Hexadecylene oxide
CN 1-Hexadecene oxide
CN CyraCure UVR 6216
CN Hexadecylene oxide
CN Tetradecyloxirane
CN UVR 6216
CN Vikolox 16
DR 151284-10-5
MF C16 H32 O
CI COM
LC STN Files: ANABSTR, BEILSTEIN*, BIOSIS, CA, CAPLUS, CASREACT,
CHEMCATS,
CHEMINFORMRX, CHEMLIST, CSCHEM, CSNB, HSDB*, IFICDB, IFIPAT,
IFIUDB,
PIRA, PROMT, RTECS*, SPECINFO, TOXCENTER, USPAT2, USPATFULL,
USPATOLD
(*File contains numerically searchable property data)
Other Sources: EINECS**, NDSL**, TSCA**
(**Enter CHEMLIST File for up-to-date regulatory information)

/ Structure 1 in file .gra /

PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

331 REFERENCES IN FILE CA (1907 TO DATE)
103 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
331 REFERENCES IN FILE CAPLUS (1907 TO DATE)

=> s 3001-72-7/rn
L5 1 3001-72-7/RN

=> d L5

L5 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2009 ACS on STN
RN ***3001-72-7*** REGISTRY
ED Entered STN: 16 Nov 1984
CN Pyrrolo[1,2-a]pyrimidine, 2,3,4,6,7,8-hexahydro- (CA INDEX NAME)
OTHER NAMES:
CN 1,5-Diazabicyclo[4.3.0]non-5-ene
CN 1,5-Diazobicyclo[4.3.0]non-5-ene
CN 2,3,4,6,7,8-Hexahydropyrrolo[1,2-a]pyrimidine
CN DBN
CN DBN (heterocycle)
CN NBU
CN NSC 118106
DR 25986-32-7, 312727-86-9
MF C7 H12 N2
CI COM
LC STN Files: ANABSTR, BEILSTEIN*, BIOSIS, CA, CAPLUS, CASREACT,

CHEMCATS,
 CHEMINFORMRX, CHEMLIST, CSCHEM, GMELIN*, IFICDB, IFIPAT, IFIUDB,
 MEDLINE, MSDS-OHS, SPECINFO, SYNTHLINE, TOXCENTER, USPAT2,
 USPATFULL,
 USPATOLD
 (*File contains numerically searchable property data)
 Other Sources: EINECS**
 (**Enter CHEMLIST File for up-to-date regulatory information)

/ Structure 2 in file .gra /

PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

1055 REFERENCES IN FILE CA (1907 TO DATE)
40 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
1056 REFERENCES IN FILE CAPLUS (1907 TO DATE)

=> d L2

L2 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2009 ACS on STN
RN ***6674-22-2*** REGISTRY
ED Entered STN: 16 Nov 1984
CN Pyrimido[1,2-a]azepine, 2,3,4,6,7,8,9,10-octahydro- (CA INDEX
NAME)
OTHER NAMES:
CN 1,8-Diaza-7-bicyclo[5.4.0]undecene
CN 1,8-Diazabicyclo[5.4.0]undec-7-ene
CN 1,8-Diazabicyclo[5.4.0]undecene-7
CN 2,3,4,6,7,8,9,10-Octahydropyrimido[1,2-a]azepine
CN Amicure DBUE
CN Dabco DBU
CN DBU
CN NSC 111184
CN NSC 230466
CN Polycat DBU
CN U-CAT SA 851
DR 51301-56-5, 69722-76-5, 78995-63-8, 83329-50-4, 31171-04-7, 41015-
70-7
MF C9 H16 N2
CI COM
LC STN Files: ANABSTR, BEILSTEIN*, BIOSIS, CA, CAPLUS, CASREACT,
CHEMCATS,
 CHEMINFORMRX, CHEMLIST, CIN, CSCHEM, GMELIN*, IFICDB, IFIPAT,
IFIUDB,
 MEDLINE, MSDS-OHS, SPECINFO, TOXCENTER, USPAT2, USPATFULL,
 USPATOLD
 (*File contains numerically searchable property data)
 Other Sources: DSL**, EINECS**, TSCA**
 (**Enter CHEMLIST File for up-to-date regulatory information)

/ Structure 3 in file .gra /

PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

3773 REFERENCES IN FILE CA (1907 TO DATE)

147 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
3786 REFERENCES IN FILE CAPLUS (1907 TO DATE)

=> d his

(FILE 'HOME' ENTERED AT 15:10:14 ON 06 MAR 2009)

FILE 'REGISTRY' ENTERED AT 15:10:28 ON 06 MAR 2009

L1 0 S 6674-22-2/CN
L2 1 S 6674-22-2/RN

FILE 'CPLUS' ENTERED AT 15:13:10 ON 06 MAR 2009

L3 3786 S L2

FILE 'REGISTRY' ENTERED AT 15:13:28 ON 06 MAR 2009

L4 1 S 7320-37-8/RN
L5 1 S 3001-72-7/RN

=> s triethylene (w) diamine
 3806 TRIETHYLENE
 438598 DIAMINE
 76 DIAMINES
 438598 DIAMINE
 (DIAMINE OR DIAMINES)
L6 98 TRIETHYLENE (W) DIAMINE

=> s 280-57-9/rn
L7 1 280-57-9/RN

=> d L7

L7 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2009 ACS on STN
RN ***280-57-9*** REGISTRY

ED Entered STN: 16 Nov 1984

CN 1,4-Diazabicyclo[2.2.2]octane (CA INDEX NAME)

OTHER NAMES:

CN 1,4-Ethlenepiperazine
CN 33LV
CN A 33
CN Activator 105E
CN Bicyclo[2.2.2]-1,4-diazaoctane
CN D 33LV
CN Dabco
CN Dabco 33LV
CN Dabco 3LV
CN DABCO Crystal
CN Dabco Crystalline
CN Dabco L 1202
CN Dabco S 25
CN Jeffcat TD 100
CN Kaoilizer 31
CN L 33
CN L 33E
CN LC 96003
CN LV 33
CN Minico L 1020
CN N,N'-endo-Ethlenepiperazine
CN Niax A 33
CN NSC 56362

CN PC CAT TD 33
CN PC-TD
CN Polycat 33LV
CN TD 100
CN TED
CN TEDA
CN Teda L 33
CN Tegamine 33
CN Tego Amine
CN Texacat TD 100
CN Texacat TD 33
CN Thancat TD 33
CN Thancat TD 33A
CN Toral SM 2
CN Toyocat L 33
CN Toyocat TEDA L 33
CN Triethylenediamine
DR 903524-95-8, 165724-47-0, 23790-33-2, 101484-19-9, 150605-01-9,
88935-43-7, 203072-11-1, 309955-09-7
MF C6 H12 N2
CI COM, RPS
LC STN Files: AGRICOLA, ANABSTR, AQUIRE, BEILSTEIN*, BIOSIS,
BIOTECHNO, CA,
CAPLUS, CASREACT, CBNB, CHEMCATS, CHEMINFORMRX, CHEMLIST, CIN,
CSChem,
CSNB, DETERM*, EMBASE, ENCOMPLIT, ENCOMPLIT2, ENCOMPPAT,
ENCOMPPAT2,
GMELIN*, HSDB*, IFICDB, IFIPAT, IFIUDB, MEDLINE, MRCK*, MSDS-OHS,
PIRA,
PROMT, RTECS*, SPECINFO, SYNTHLINE, TOXCENTER, ULIDAT, USPAT2,
USPATFULL, USPATOLD
(*File contains numerically searchable property data)
Other Sources: DSL**, EINECS**, TSCA**
(**Enter CHEMLIST File for up-to-date regulatory information)

/ Structure 4 in file .gra /

PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

6376 REFERENCES IN FILE CA (1907 TO DATE)
301 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
6392 REFERENCES IN FILE CAPLUS (1907 TO DATE)

=> d his

FILE 'HOME' ENTERED AT 15:10:14 ON 06 MAR 2009
FILE 'REGISTRY' ENTERED AT 15:10:28 ON 06 MAR 2009
L1 0 S 6674-22-2/CN
L2 1 S 6674-22-2/RN
FILE 'CAPLUS' ENTERED AT 15:13:10 ON 06 MAR 2009
L3 3786 S L2
FILE 'REGISTRY' ENTERED AT 15:13:28 ON 06 MAR 2009
L4 1 S 7320-37-8/RN
L5 1 S 3001-72-7/RN

L6 98 S TRIETHYLENE (W) DIAMINE
L7 1 S 280-57-9/RN

=> file caplus uspatfull
COST IN U.S. DOLLARS
SINCE FILE
ENTRY
TOTAL
SESSION
FULL ESTIMATED COST 21.78 30.25

FILE 'CAPLUS' ENTERED AT 15:16:58 ON 06 MAR 2009
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FILE 'USPATFULL' ENTERED AT 15:16:58 ON 06 MAR 2009
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=> s (L2 OR L5 OR L7) AND L4
L8 4 (L2 OR L5 OR L7) AND L4

=> d L8 1-4 ti ibib

L8 ANSWER 1 OF 4 CAPLUS COPYRIGHT 2009 ACS on STN
TI Hydrocarbon desulfurization with mercaptan removal by treatment
with

alicyclic tertiary amines and nucleophilic acceptors
ACCESSION NUMBER: 2005:1027004 CAPLUS <<LOGINID::20090306>>

DOCUMENT NUMBER: 143:328922

TITLE: Hydrocarbon desulfurization with mercaptan
removal by

treatment with alicyclic tertiary amines and
nucleophilic acceptors

INVENTOR(S): Schield, John A.; Cappel, Weldon John

PATENT ASSIGNEE(S): Baker Hughes Incorporated, USA

SOURCE: PCT Int. Appl., 23 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent

LANGUAGE: English

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
-----	---	-----	-----	-----
WO 2005087899 20040211	A1	20050922	WO 2004-US4011	
W:	AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, GD, LC, NI, SY, ZW, AZ,		GE, GH, GM, HR, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, RW: BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK,	

EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI,
SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN,
TD, TG CA 2554548 A1 20050922 CA 2004-2554548
20040211 EP 1713885 A1 20061025 EP 2004-710238
20040211 R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC,
PT, IE, SI, FI, RO, CY, TR, BG, CZ, EE, HU, SK
US 20070142244 A1 20070621 US 2006-588341
20060803
PRIORITY APPLN. INFO.: WO 2004-US4011 W
20040211
OTHER SOURCE(S): MARPAT 143:328922
REFERENCE COUNT: 5 THERE ARE 5 CITED REFERENCES AVAILABLE
FOR THIS
RECORD. ALL CITATIONS AVAILABLE IN THE RE
FORMAT

L8 ANSWER 2 OF 4 CAPLUS COPYRIGHT 2009 ACS on STN
TI Study of the structure-reactivity relationships in the
photoinitiated
cationic polymerization of epoxide monomers
ACCESSION NUMBER: 1998:808928 CAPLUS <<LOGINID::20090306>>
DOCUMENT NUMBER: 130:182793
TITLE: Study of the structure-reactivity relationships
in the photoinitiated cationic polymerization of
epoxide monomers
AUTHOR(S): Crivello, James V.; Linzer, Volker
CORPORATE SOURCE: Polymer Synthesis Center, Department of
Chemistry, Rensselaer Polytechnic Institute, Troy, NY,
12180-3590, USA
SOURCE: Polimery (Warsaw) (1998), 43(11/12), 661-672
PUBLISHER: Instytut Chemii Przemyslowej
DOCUMENT TYPE: Journal
LANGUAGE: English
REFERENCE COUNT: 21 THERE ARE 21 CITED REFERENCES AVAILABLE
FOR THIS
RECORD. ALL CITATIONS AVAILABLE IN THE RE
FORMAT

L8 ANSWER 3 OF 4 CAPLUS COPYRIGHT 2009 ACS on STN
TI Grease-compatible, hydrolytically stable encapsulant compositions
for use
in signal transmission devices
ACCESSION NUMBER: 1991:103808 CAPLUS <<LOGINID::20090306>>
DOCUMENT NUMBER: 114:103808
ORIGINAL REFERENCE NO.: 114:17695a, 17698a
TITLE: Grease-compatible, hydrolytically stable
encapsulant
devices
INVENTOR(S): Croft, Thomas S.; Haugen, Hartwick A.

PATENT ASSIGNEE(S): Minnesota Mining and Manufacturing Co., USA
 SOURCE: Eur. Pat. Appl., 26 pp.
 DOCUMENT TYPE: Patent
 LANGUAGE: English
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
EP 372747	A2	19900613	EP 1989-312078	
19891121				
EP 372747	A3	19901010		
EP 372747	B1	19950823		
R: AT, CH, DE, ES, FR, GB, IT, LI, SE				
AU 8945338	A	19900531	AU 1989-45338	
19891120				
AU 620662	B2	19920220		
ES 2076218	T3	19951101	ES 1989-312078	
19891121				
CA 2003781	A1	19900525	CA 1989-2003781	
19891124				
CA 2003781	C	19990216		
JP 02212580	A	19900823	JP 1989-306376	
19891124				
JP 2772075	B2	19980702		
KR 135973	B1	19980424	KR 1989-17080	
19891124				
BR 8905961	A	19900619	BR 1989-5961	
19891127				
PRIORITY APPLN. INFO.:			US 1988-274337	A
19881125				

L8 ANSWER 4 OF 4 USPATFULL on STN
 TI Encapsulant compositions for use in signal transmission devices
 ACCESSION NUMBER: 91:5171 USPATFULL <>LOGINID::20090306>>
 TITLE: Encapsulant compositions for use in signal
 transmission
 devices
 INVENTOR(S): Croft, Thomas S., Austin, TX, United States
 Haugen, Hartwick, Austin, TX, United States
 PATENT ASSIGNEE(S): Minnesota Mining and Manufacturing, St. Paul,
 MN,
 United States (U.S. corporation)

NUMBER	KIND	DATE
US 4985475		19910115
US 1988-274337		19881125 (7)
RELATED APPLN. INFO.:		Continuation-in-part of Ser. No. US 1987-19295, filed
DOCUMENT TYPE:		on 9 Mar 1987, now patented, Pat. No. US 4857563
FILE SEGMENT:		Utility
PRIMARY EXAMINER:		Granted
ASSISTANT EXAMINER:		Schofer, Joseph L.
LEGAL REPRESENTATIVE:		Mulcahy, Peter D.
NUMBER OF CLAIMS:		Sell, D. M., Lilly, J. V.
EXEMPLARY CLAIM:		17
		1

LINE COUNT: 1302
CAS INDEXING IS AVAILABLE FOR THIS PATENT.

=> d 1-4 hit, bib

L8 ANSWER 1 OF 4 CAPLUS COPYRIGHT 2009 ACS on STN
IT ***280-57-9*** , 1,4-Diazabicyclo[2.2.2]octane ***3001-72-7***
'
1,5-Diazabicyclo[4.3.0]non-5-ene ***6674-22-2*** ,
1,8-Diazabicyclo[5.4.0]undec-7-ene
RL: CPS (Chemical process); PEP (Physical, engineering or chemical
process); PROC (Process)
(hydrocarbon desulfurization with mercaptan removal by treatment
with
alicyclic tertiary amines and nucleophilic acceptors)
IT 463-73-0D, Chloroformic acid, compds. 2817-45-0D, Phosphoramicidic
acid,
compds. ***7320-37-8*** , 1,2-Epoxyhexadecane 19270-07-6D,
Cyanoformic acid, compds.
RL: CPS (Chemical process); PEP (Physical, engineering or chemical
process); PROC (Process)
(nucleophilic acceptors; hydrocarbon desulfurization with
mercaptan
removal by treatment with alicyclic tertiary amines and
nucleophilic
acceptors)
AN 2005:1027004 CAPLUS <>LOGINID::20090306>>
DN 143:328922
TI Hydrocarbon desulfurization with mercaptan removal by treatment
with
alicyclic tertiary amines and nucleophilic acceptors
IN Schield, John A.; Cappel, Weldon John
PA Baker Hughes Incorporated, USA
SO PCT Int. Appl., 23 pp.
CODEN: PIXXD2
DT Patent
LA English
FAN.CNT 1
PATENT NO. KIND DATE APPLICATION NO. DATE

PI WO 2005087899 A1 20050922 WO 2004-US4011
20040211 W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA,
CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB,
GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ,
LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA,
NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL,
SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM,
ZW
RW: BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM,
AZ,
EE, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK,

ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI,
SK,
TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN,
TD, TG
CA 2554548 A1 20050922 CA 2004-2554548
20040211 EP 1713885 A1 20061025 EP 2004-710238
20040211

R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC,
PT,
IE, SI, FI, RO, CY, TR, BG, CZ, EE, HU, SK
US 20070142244 A1 20070621 US 2006-588341
20060803
PRAI WO 2004-US4011 W 20040211
OS MARPAT 143:328922
RE.CNT 5 THERE ARE 5 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L8 ANSWER 2 OF 4 CAPLUS COPYRIGHT 2009 ACS on STN
IT 108-87-2, 1-Methylcyclohexane 291-64-5, Cycloheptane ***6674-
22-2***
, 1,8-Diazabicyclo[5.4.0]undec-7-ene 10353-53-4, 1,2-Epoxyhex-5-
ene 55334-42-4, 1,2-Dibromododecane 85721-25-1
RL: RCT (Reactant); RACT (Reactant or reagent)
(reactant in monomer prepn.; structure effect on kinetics of
photoinitiated cationic polymn. of epoxides)
IT 285-67-6, Epoxycyclopentane 286-20-4, 7-Oxabicyclo[4.1.0]heptane
286-62-4, Epoxycyclooctane 1436-34-6 1464-53-5, 2,2'-Bioxirane
1502-29-0, cis-Epoxycyclododecane 1686-14-2, .alpha.-Pinene oxide
1758-33-4, cis-2,3-Epoxybutane 2404-44-6 2426-07-5 2855-19-8
2984-50-1 3234-28-4 4683-60-7, trans-Epoxycyclododecane
7320-37-8 21490-63-1, trans-2,3-Epoxybutane
RL: PRP (Properties); RCT (Reactant); RACT (Reactant or reagent)
(structure effect on kinetics of photoinitiated cationic polymn.

of
epoxides)
AN 1998:808928 CAPLUS <<LOGINID::20090306>>
DN 130:182793
TI Study of the structure-reactivity relationships in the
photoinitiated
cationic polymerization of epoxide monomers
AU Crivello, James V.; Linzer, Volker
CS Polymer Synthesis Center, Department of Chemistry, Rensselaer
Polytechnic
Institute, Troy, NY, 12180-3590, USA
SO Polimery (Warsaw) (1998), 43(11/12), 661-672
CODEN: POLIA4; ISSN: 0032-2725
PB Instytut Chemii Przemyslowej
DT Journal
LA English

RE.CNT 21 THERE ARE 21 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L8 ANSWER 3 OF 4 CAPLUS COPYRIGHT 2009 ACS on STN
IT 101-34-8, Flexircin P 8 112-75-4 1191-43-1, 1,6-Hexanedithiol
3319-31-1 3489-28-9, 1,9-Nonanedithiol ***6674-22-2***
7320-37-8 , Vikalox 16 9044-17-1, Indopol H 100 10482-
56-1 25085-98-7, ERL 4221 25155-23-1, Trixylenyl phosphate 25231-21-

25266-02-8, PA-18 26616-47-7, ERL 4234 37226-48-5, Araldite
 53564-35-5, Escopol R020 81647-91-8, Paol 40 132325-11-2,
FuelSaver
 RL: USES (Uses)
 (encapsulation compns. contg., grease-compatible, hydrolytically
 stable, for signal transmission devices)
 AN 1991:103808 CAPLUS <>LOGINID:20090306>>
 DN 114:103808
 OREF 114:17695a,17698a
 TI Grease-compatible, hydrolytically stable encapsulant compositions
 for use
 in signal transmission devices
 IN Croft, Thomas S.; Haugen, Hartwick A.
 PA Minnesota Mining and Manufacturing Co., USA
 SO Eur. Pat. Appl., 26 pp.
 CODEN: EPXXDW
 DT Patent
 LA English
 FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI EP 372747 19891121	A2	19900613	EP 1989-312078	
EP 372747	A3	19901010		
EP 372747	B1	19950823		
R: AT, CH, DE, ES, FR, GB, IT, LI, SE AU 8945338	A	19900531	AU 1989-45338	
19891120				
AU 620662	B2	19920220		
ES 2076218	T3	19951101	ES 1989-312078	
19891121				
CA 2003781	A1	19900525	CA 1989-2003781	
19891124				
CA 2003781	C	19990216		
JP 02212580	A	19900823	JP 1989-306376	
19891124				
JP 2772075	B2	19980702		
KR 135973	B1	19980424	KR 1989-17080	
19891124				
BR 8905961	A	19900619	BR 1989-5961	
19891127				
PRAI US 1988-274337	A	19881125		
L8 ANSWER 4 OF 4 USPATFULL on STN				
IT 101-34-8, Flexicrin P 8 112-75-4 1191-43-1, 1,6-Hexanedithiol 3319-31-1 3489-28-9, 1,9-Nonanedithiol ***6674-22-2*** ***7320-37-8*** , Vikolox 16 9044-17-1, Indopol H 100				
10482-56-1				
25085-98-7, ERL 4221 25155-23-1, Trixylenyl phosphate 25231-				
21-4				
25266-02-8, PA-18 26616-47-7, ERL 4234 37226-48-5, Araldite 53564-35-5, Escopol R020 81647-91-8, Paol 40 132325-11-2, FuelSaver (encapsulation compns. contg., grease-compatible, hydrolytically stable, for signal transmission devices)				
AN 91:5171 USPATFULL <>LOGINID:20090306>>				
TI Encapsulant compositions for use in signal transmission devices				
IN Croft, Thomas S., Austin, TX, United States				

Haugen, Hartwick, Austin, TX, United States
PA Minnesota Mining and Manufacturing, St. Paul, MN, United States
(U.S.
corporation)
PI US 4985475 19910115
AI US 1988-274337 19881125 (7)
RLI Continuation-in-part of Ser. No. US 1987-19295, filed on 9 Mar
1987, now
patented, Pat. No. US 4857563
DT Utility
FS Granted
EXNAM Primary Examiner: Schofer, Joseph L.; Assistant Examiner:
Mulcahy, Peter
D.
LREP Sell, D. M., Lilly, J. V.
CLMN Number of Claims: 17
ECL Exemplary Claim: 1
DRWN No Drawings
LN.CNT 1302
CAS INDEXING IS AVAILABLE FOR THIS PATENT.

=> s (L2 OR L5 OR L7) AND thiolysis
L9 3 (L2 OR L5 OR L7) AND THIOLYSIS

=> d L9 1-3 hit, ibib

L9 ANSWER 1 OF 3 CAPLUS COPYRIGHT 2009 ACS on STN
ST siloxane tetrahydro hydrogen rich prepn alcoholysis dihalosilane
pyridine
complex; alkylthio disilathiane tetrahydro hydrogen rich prepn
thiolysis dihalosilane complex; process prepn hydrogen
rich
siloxane disilathiane alcoholysis ***thiolysis*** dihalosilane
IT Amines, preparation
RL: RCT (Reactant); SPN (Synthetic preparation); PREP
(Preparation); RACT
(Reactant or reagent)
(complexes, silicon; process for prepn. of hydrogen-rich
1,1,3,3-tetrahydrodisiloxanes and -disilathianes by alcoholysis
and
thiolysis of dihalosilane pyridine complexes)
IT Siloxanes (nonpolymeric)
RL: SPN (Synthetic preparation); PREP (Preparation)
(disiloxanes, hydrogen-rich; process for prepn. of hydrogen-rich
1,1,3,3-tetrahydrodisiloxanes and -disilathianes by alcoholysis
and
thiolysis of dihalosilane pyridine complexes)
IT Alcoholysis
(process for prepn. of hydrogen-rich 1,1,3,3-
tetrahydrodisiloxanes and
-disilathianes by alcoholysis and ***thiolysis*** of
dihalosilane
pyridine complexes)
IT Group IVA element compounds
Group VIA element compounds
RL: SPN (Synthetic preparation); PREP (Preparation)
(silathianes, 1,3-disilathianes; process for prepn. of hydrogen-
rich
1,1,3,3-tetrahydrodisiloxanes and -disilathianes by alcoholysis

and

 thiolysis of dihalosilane pyridine complexes)

IT Alcohols, reactions

 Thiols, reactions

 RL: RCT (Reactant); RACT (Reactant or reagent)

 (tertiary; process for prepn. of hydrogen-rich

 1,1,3,3-tetrahydrodisiloxanes and -disilathianes by alcoholysis

and

 thiolysis of dihalosilane pyridine complexes)

IT Solvolytic

 (***thiolysis*** ; process for prepn. of hydrogen-rich

 1,1,3,3-tetrahydrodisiloxanes and -disilathianes by alcoholysis

and

 thiolysis of dihalosilane pyridine complexes)

IT 953776-96-0P

 RL: PRPH (Prophetic); RCT (Reactant); SPN (Synthetic preparation);

PREP

 (Preparation); RACT (Reactant or reagent)

 (process for prep. of hydrogen-rich 1,1,3,3-

 tetrahydrodisiloxanes and

 -disilathianes by alcoholysis and ***thiolysis*** of

 dihalosilane

 pyridine complexes)

IT 75-65-0, tert-Butanol, reactions 75-66-1, tert-Butylmercaptan

75-85-4,

 tert-Amyl alcohol 77-74-7 100-43-6, 4-Vinylpyridine 108-47-4,

 2,4-Dimethylpyridine 108-89-4, 4-Methylpyridine 108-99-6,

 3-Methylpyridine 109-06-8, 2-Methylpyridine 110-86-1, Pyridine,

 reactions 536-75-4, 4-Ethylpyridine 590-36-3 590-67-0 594-

83-2

 595-41-5 597-05-7 597-49-9 597-93-3 598-01-6 626-55-1,

 3-Bromopyridine 690-37-9 702-81-8, 3-Methyl-1-adamantanol

768-95-6,

 Tricyclo[3.3.1.1.3,7]decan-1-ol 880-49-9, 3-Isopropyl-1-

adamantanol

 1122-58-3 1462-03-9, 1-Methylcyclopentanol 1569-44-4 1569-46-

6

 1604-02-0 1633-97-2 1639-01-6 1639-03-8 1679-09-0 1940-

18-7,

 1-Ethylcyclohexanol 3742-85-6 3761-94-2 3978-81-2,

 4-tert-Butylpyridine 4109-96-0, Dichlorosilane 5445-24-9

5827-80-5

 17257-32-8 20534-58-1, Bicyclo[2.2.2]octan-1-ol 23511-76-4

71897-97-7 74356-31-3 87383-23-1 91337-12-1 108836-86-8

116436-16-9 124547-52-0 186365-89-9 189394-12-5 200403-44-7

RL: RCT (Reactant); RACT (Reactant or reagent)

 (process for prepn. of hydrogen-rich 1,1,3,3-

 tetrahydrodisiloxanes and

 -disilathianes by alcoholysis and ***thiolysis*** of

 dihalosilane

 pyridine complexes)

IT 75-50-3, Trimethylamine, reactions 79-55-0,

 1,2,2,6,6-Pentamethylpiperidine 100-76-5, 1-Azabicyclo[2.2.2]

octane

 102-82-9, Tributylamine 121-44-8, Triethylamine, reactions

 280-57-9 , 1,4-Diazabicyclo[2.2.2]octane ***3001-72-7***

1,5-Diazabicyclo[4.3.0]non-5-ene 4458-31-5 5807-14-7,

1,5,7-Triazabicyclo[4.4.0]dec-5-ene ***6674-22-2*** ,

1,8-Diazabicyclo[5.4.0]undec-7-ene 20634-92-8 84030-20-6,

7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene
 RL: RGT (Reagent); RACT (Reactant or reagent)
 (process for prepn. of hydrogen-rich 1,1,3,3-
 tetrahydrodisiloxanes and
 -disilathianes by alcoholysis and ***thiolysis*** of
 dihalosilane
 pyridine complexes)
 IT 1002788-53-5P 1002788-54-6P 1002788-55-7P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (process for prepn. of hydrogen-rich 1,1,3,3-
 tetrahydrodisiloxanes and
 -disilathianes by alcoholysis and ***thiolysis*** of
 dihalosilane
 pyridine complexes)
 ACCESSION NUMBER: 2008:90945 CAPLUS <<LOGINID::20090306>>
 DOCUMENT NUMBER: 148:168827
 TITLE: Process for preparation of novel hydrogen-rich
 1,1,3,3-tetrahydro-1,3-disiloxanes and
 1,3-disilathianes as precursors for
 hydrosilylation,
 polymerization and material modifiers
 INVENTOR(S): Fester, Gerrit; Roewer, Gerhard; Kroke, Edwin
 PATENT ASSIGNEE(S): Technische Universitaet Bergakademie Freiberg,
 Germany
 SOURCE: PCT Int. Appl., 20pp.
 CODEN: PIXXD2
 DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
-----	-----	-----	-----	-----
WO 2008009680 20070717	A1	20080124	WO 2007-EP57379	
CA, FI, KG, ME, PL, TN, RW: IE, BF, BW, AZ, PRIORITY APPLN. INFO.: 20060717	W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW RW: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, BY, KG, KZ, MD, RU, TJ, TM			
			DE 2006-102006034336A	

OTHER SOURCE(S): CASREACT 148:168827; MARPAT 148:168827
REFERENCE COUNT: 1 THERE ARE 1 CITED REFERENCES AVAILABLE
FOR THIS
FORMAT RECORD. ALL CITATIONS AVAILABLE IN THE RE

L9 ANSWER 2 OF 3 CAPLUS COPYRIGHT 2009 ACS on STN
TI Improved process for preparation of hydrosilanes containing alkoxy, amino
and thiolato groups by alcoholysis, aminolysis and
thiolysis of
halosilanes in the presence of tertiary amine bases
ST silane hydrosilane alkoxy amino thiolate prepn process; alcoholysis
aminolysis ***thiolysis*** chlorosilane tertiary amine base
process
IT Silanes
RL: SPN (Synthetic preparation); TEM (Technical or engineered
material
use); PREP (Preparation); USES (Uses)
(alkoxy, hydrosilanes; process for prepn. of hydrosilanes contg.
alkoxy, amino and thioether substituents by alcoholysis,
aminolysis and
thiolysis of halosilanes in presence of tertiary amine
base)
IT Silanes
RL: RCT (Reactant); RACT (Reactant or reagent)
(halosilanes, hydrosilanes; process for prepn. of hydrosilanes
contg.
alkoxy, amino and thioether substituents by alcoholysis,
aminolysis and
thiolysis of halosilanes in presence of tertiary amine
base)
IT Thioethers
RL: SPN (Synthetic preparation); TEM (Technical or engineered
material
use); PREP (Preparation); USES (Uses)
(hydrosilane; process for prepn. of hydrosilanes contg. alkoxy,
amino
and thioether substituents by alcoholysis, aminolysis and
thiolysis of halosilanes in presence of tertiary amine
base)
IT Silanes
RL: RCT (Reactant); SPN (Synthetic preparation); TEM (Technical or
engineered material use); PREP (Preparation); RACT (Reactant or
reagent);
USES (Uses)
(hydrosilanes; process for prepn. of hydrosilanes contg. alkoxy,
amino
and thioether substituents by alcoholysis, aminolysis and
thiolysis of halosilanes in presence of tertiary amine
base)
IT Silazanes
RL: SPN (Synthetic preparation); TEM (Technical or engineered
material
use); PREP (Preparation); USES (Uses)
(hydrosilanes; process for prepn. of hydrosilanes contg. alkoxy,
amino
and thioether substituents by alcoholysis, aminolysis and
thiolysis of halosilanes in presence of tertiary amine
base)

IT 56-24-6 64-17-5, Ethanol, reactions 67-56-1, Methanol, reactions
 67-63-0, Isopropanol, reactions 71-23-8, 1-Propanol, reactions
 71-36-3, 1-Butanol, reactions 71-41-0, 1-Pentanol, reactions
 75-08-1,
 Ethanethiol 75-33-2, 2-Propanethiol 76-84-6, Triphenylmethanol
 76-87-9 78-83-1, Isobutanol, reactions 96-41-3, Cyclopentanol
 98-85-1 100-51-6, Benzenemethanol, reactions 103-49-1,
Dibenzylamine
 107-03-9, 1-Propanethiol 107-18-6, Allyl alcohol, reactions
 107-19-7,
 2-Propyn-1-ol 108-18-9, Diisopropylamine 108-89-4, 4-
Methylpyridine
 108-93-0, Cyclohexanol, reactions 108-95-2, Phenol, reactions
 108-98-5, Benzenethiol, reactions 109-79-5, 1-Butanethiol 109-
 89-7,
 Diethylamine, reactions 110-89-4, Piperidine, reactions 110-96-
 3,
 Disobutylamine 111-92-2, Dibutylamine 115-19-5 123-51-3
 123-75-1,
 Pyrrolidine, reactions 142-84-7, Dipropylamine 513-42-8 513-
 44-0
 583-59-5, 2-Methylcyclohexanol 597-52-4, Triethylsilanol 598-
 32-3,
 3-Buten-2-ol 627-27-0, 3-Buten-1-ol 764-01-2, 2-Butyn-1-ol
 791-31-1
 894-08-6 927-74-2, 3-Butyn-1-ol 994-32-1 1066-40-6,
Trimethylsilanol
 1067-96-5 1067-97-6 1189-31-7 1529-27-7, Triphenylgermanol
 1529-35-7 1569-69-3, Cyclohexanethiol 1679-07-8,
Cyclopentanethiol
 2028-63-9, 3-Butyn-2-ol 2216-51-5, (-)-Menthol 2622-89-1,
Borinic
 acid, diphenyl- 2628-46-8 3695-77-0 4109-96-0, Dichlorosilane
 4237-48-3 4426-31-7 4453-82-1 4631-63-4 5337-72-4 5906-
 79-6
 6117-91-5, 2-Buten-1-ol 6300-99-8 13061-97-7 13121-70-5
 15356-60-2, (+)-Menthol 17546-98-4, Trimethylplumbanol 17687-
 73-9
 17687-74-0 17877-23-5 17888-60-7 18388-85-7 18547-88-1,
 Tricyclohexylsilanol 26819-05-6 36633-36-0 52102-16-6
 55999-97-8
 56889-90-8, Tri-tert-butylsilanol 66952-11-2 82490-11-7
 96383-35-6
 98156-23-1 104503-69-7 118978-84-0 134178-80-6 171503-79-0
 228092-38-4 317374-14-4 718642-35-4 855637-46-6 860704-01-4
 952755-22-5 952755-23-6 952755-24-7 952755-25-8 952755-26-9
 952755-27-0 952755-28-1 952755-29-2 952755-30-5 952755-31-6
 952755-32-7 952755-33-8 952755-34-9
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (process for prepn. of hydrosilanes contg. alkoxy, amino and
 thioether
 substituents by alcoholysis, aminolysis and ***thiolysis***
 of
 halosilanes in presence of tertiary amine base)
 IT 952755-20-3P 952755-21-4P 953776-96-0P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP
 (Preparation); RACT
 (Reactant or reagent)
 (process for prepn. of hydrosilanes contg. alkoxy, amino and

thioether
 substituents by alcoholysis, aminolysis and ***thiolysis***
 of
 halosilanes in presence of tertiary amine base)
 IT 75-50-3, Trimethylamine, reactions 110-86-1, Pyridine, reactions
 121-44-8, Triethylamine, reactions ***280-57-9*** ,
 1,4-Diazabicyclo[2.2.2]octane 289-95-2, Pyrimidine 290-37-9,
 Pyrazine
 3001-72-7 4458-31-5 ***6674-22-2*** , DBU 20634-
 92-8
 RL: RGT (Reagent); RACT (Reactant or reagent)
 (process for prepn. of hydrosilanes contg. alkoxy, amino and
 thioether
 substituents by alcoholysis, aminolysis and ***thiolysis***
 of
 halosilanes in presence of tertiary amine base)
 IT 1507-99-9P 2487-90-3P 5314-52-3P 6675-79-2P 18165-68-9P
 18165-77-0P 20114-49-2P 27804-64-4P 38442-21-6P,
 Diphenoxysilane
 149578-93-8P 220214-19-7P 859765-44-9P 952755-06-5P 952755-
 07-6P
 952755-08-7P 952755-09-8P 952755-10-1P 952755-11-2P 952755-
 12-3P
 952755-13-4P 952755-14-5P 952755-15-6P 952755-16-7P 952755-
 17-8P
 952755-18-9P 952755-19-0P
 RL: SPN (Synthetic preparation); TEM (Technical or engineered
 material
 use); PREP (Preparation); USES (Uses)
 (process for prepn. of hydrosilanes contg. alkoxy, amino and
 thioether
 substituents by alcoholysis, aminolysis and ***thiolysis***
 of
 halosilanes in presence of tertiary amine base)
 ACCESSION NUMBER: 20071204421 CAPLUS <<LOGINID::20090306>>
 DOCUMENT NUMBER: 147:486546
 TITLE: Improved process for preparation of
 hydrosilanes
 containing alkoxy, amino and thiolato groups by
 alcoholysis, aminolysis and ***thiolysis***
 of
 halosilanes in the presence of tertiary amine
 bases
 INVENTOR(S): Fester, Gerrit; Roewer, Gerhard; Kroke, Edwin
 PATENT ASSIGNEE(S): Technische Universitaet Bergakademie Freiberg,
 Germany
 SOURCE: PCT Int. Appl., 43pp.
 CODEN: PIXXD2
 DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
-----	-----	-----	-----	-----
WO 2007118474	A2	20071025	WO 2007-DE724	
20070419				
WO 2007118474	A3	20071221		
	W:	AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ,		

CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI,
 GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG,
 KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, MG,
 MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT,
 RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR,
 TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW
 RW: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU,
 IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR,
 BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG,
 BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM,
 AZ, BY, KG, KZ, MD, RU, TJ, TM, AP, EA, EP, OA
 DE 102006019016 A1 20071025 DE 2006-102006019016
 20060419 PRIORITY APPLN. INFO.: DE 2006-102006019016A
 20060419 DE 2006-102006034335A
 20060717
 OTHER SOURCE(S): CASREACT 147:486546; MARPAT 147:486546

L9 ANSWER 3 OF 3 CAPLUS COPYRIGHT 2009 ACS on STN
 IT Solvolysis catalysts
 (***thiolyisis*** ; compn. for depilation contg. complexes of
 aluminum or zinc complexes with thioglycolic acid)
 IT 102-71-6, Triethanolamine, biological studies ***280-57-9*** ,
 1,4-Diazabicyclo[2.2.2]octane ***6674-22-2*** ,
 1,8-Diazabicyclo[5.4.0]undec-7-ene
 RL: CAT (Catalyst use); COS (Cosmetic use); BIOL (Biological
 study); USES
 (Uses)
 (compn. for depilation contg. complexes of aluminum or zinc
 complexes
 with thioglycolic acid)
 ACCESSION NUMBER: 2006:1354152 CAPLUS <<LOGINID::20090306>>
 DOCUMENT NUMBER: 146:106772
 TITLE: Composition for depilation containing complexes
 of aluminum or zinc complexes with thioglycolic
 acid
 INVENTOR(S): Marte, Walter; Meyer, Martin; Dutler, Hans;
 Zimmermann, Michael
 PATENT ASSIGNEE(S): Tex-A-Tec AG, Switz.
 SOURCE: PCT Int. Appl., 47pp.
 CODEN: PIXXD2
 DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 2
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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WO 2006136441 A1 20061228 WO 2006-EP6080
20060623
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA,
CH,
CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB,
GD,
GE, GH, GM, HN, HR, ID, IL, IN, IS, JP, KE, KG, KM, KN,
KP,
KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK,
MN,
MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS,
RU,
SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA,
UG,
US, UZ, VC, VN, ZA, ZM, ZW
RW: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU,
IE,
IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF,
BJ,
CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG, BW,
GH,
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ,
BY,
KG, KZ, MD, RU, TJ, TM
EP 1736207 A1 20061227 EP 2005-13593
20050623
R: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU,
IE,
IS, IT, LI, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, AL,
BA,
HR, LV, MK, YU
EP 1779899 A1 20070502 EP 2005-26090
20051130
R: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU,
IE,
IS, IT, LI, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR,
AL,
BA, HR, MK, YU
EP 1917073 A1 20080507 EP 2006-762166
20060623
R: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU,
IE,
IS, IT, LI, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR
PRIORITY APPLN. INFO.: EP 2005-13593 A
20050623
EP 2005-26090 A
20051130
WO 2006-EP6080 W
20060623
REFERENCE COUNT: 7 THERE ARE 7 CITED REFERENCES AVAILABLE
FOR THIS
RECORD. ALL CITATIONS AVAILABLE IN THE RE
FORMAT

=> s (L2 OR L5 OR L7) AND epoxide

L10 489 (L2 OR L5 OR L7) AND EPOXIDE

=> s L10 and (mercaptan OR thiol)

L11 85 L10 AND (MERCAPTAN OR THIOL)

=> d L11 1-85 ti

L11 ANSWER 1 OF 85 CAPLUS COPYRIGHT 2009 ACS on STN
TI Process for preparation of substituted 2-aminoethylsulfonic acids

L11 ANSWER 2 OF 85 CAPLUS COPYRIGHT 2009 ACS on STN
TI Tertiary amines as highly efficient catalysts in the ring-opening
reactions of ***epoxides*** with amines or ***thiols*** in
H2O:
expeditious approach to .beta.-amino alcohols and .beta.-
aminothioethers

L11 ANSWER 3 OF 85 CAPLUS COPYRIGHT 2009 ACS on STN
TI Hydrocarbon desulfurization with ***mercaptan*** removal by
treatment
with alicyclic tertiary amines and nucleophilic acceptors

L11 ANSWER 4 OF 85 CAPLUS COPYRIGHT 2009 ACS on STN
TI Artificial neural network for predicting the toxicity of organic
molecules

L11 ANSWER 5 OF 85 CAPLUS COPYRIGHT 2009 ACS on STN
TI Regio- and stereospecific synthesis of (O-TIPS)-protected
2-hydroxyalkylmercaptans from ***epoxides*** and
triisopropylsilanethiol

L11 ANSWER 6 OF 85 CAPLUS COPYRIGHT 2009 ACS on STN
TI Reaction of 1,2-dioxetanes with heteroatom nucleophiles: adduct
formation
by nucleophilic attack at the peroxide bond

L11 ANSWER 7 OF 85 CAPLUS COPYRIGHT 2009 ACS on STN
TI Polymercaptan-fused ring amine catalysts for curing epoxy resins

L11 ANSWER 8 OF 85 USPATFULL on STN
TI ORGANOMETALLIC COMPOSITIONS AND COATING COMPOSITIONS

L11 ANSWER 9 OF 85 USPATFULL on STN
TI Thiourethane Compositions and Processes for Making and Using Same

L11 ANSWER 10 OF 85 USPATFULL on STN
TI SEQUENTIAL ANALYSIS OF BIOLOGICAL SAMPLES

L11 ANSWER 11 OF 85 USPATFULL on STN
TI SEQUENTIAL ANALYSIS OF BIOLOGICAL SAMPLES

L11 ANSWER 12 OF 85 USPATFULL on STN
TI Method of producing flexible laminates

L11 ANSWER 13 OF 85 USPATFULL on STN
TI Synthesis and Applications of 2-Oxo-4-Methylthiobutyric Acid, Its
Salts
and Its Derivatives

L11 ANSWER 14 OF 85 USPATFULL on STN
TI FLUORESCENT BIOMOLECULE LABELING REAGENTS

L11 ANSWER 15 OF 85 USPATFULL on STN

TI Process of Preparing Esters and Ethers of Probucol and
Derivatives
Thereof

L11 ANSWER 16 OF 85 USPATFULL on STN
TI Hardener for Epoxy Resin and Epoxy Resin Composition

L11 ANSWER 17 OF 85 USPATFULL on STN
TI MICROBIAL TRANSFORMATION METHOD FOR THE PREPARATION OF AN
EPOTHILONE

L11 ANSWER 18 OF 85 USPATFULL on STN
TI ***MERCAPTAN*** -HARDENED EPOXY POLYMER COMPOSITIONS AND
PROCESSES
FOR MAKING AND USING SAME

L11 ANSWER 19 OF 85 USPATFULL on STN
TI POLYMER COMPOSITIONS AND PROCESSES FOR MAKING AND USING SAME

L11 ANSWER 20 OF 85 USPATFULL on STN
TI Copper-catalyzed formation of carbon-heteroatom and carbon-carbon
bonds

L11 ANSWER 21 OF 85 USPATFULL on STN
TI ORGANOMETALLIC COMPOSITIONS AND COATING COMPOSITIONS

L11 ANSWER 22 OF 85 USPATFULL on STN
TI Pyrrolotriazine inhibitors of kinases

L11 ANSWER 23 OF 85 USPATFULL on STN
TI Polythiopropene compositions and processes for making and using
same

L11 ANSWER 24 OF 85 USPATFULL on STN
TI Retroviral protease inhibitors

L11 ANSWER 25 OF 85 USPATFULL on STN
TI Retroviral protease inhibitors

L11 ANSWER 26 OF 85 USPATFULL on STN
TI ***Thiol*** ester compositions and processes for making and
using
same

L11 ANSWER 27 OF 85 USPATFULL on STN
TI Organometallic compositions and coating compositions

L11 ANSWER 28 OF 85 USPATFULL on STN
TI Pyrrolotriazine inhibitors of kinases

L11 ANSWER 29 OF 85 USPATFULL on STN
TI Controlled release fertilizer material and process for production
thereof

L11 ANSWER 30 OF 85 USPATFULL on STN
TI Pyrrolotriazine inhibitors of kinases

L11 ANSWER 31 OF 85 USPATFULL on STN
TI Process of preparing esters and ethers of probucol and
derivatives

thereof

L11 ANSWER 32 OF 85 USPATFULL on STN
TI Radiation-curable coatings for plastic substrates from
multifunctional
acrylate oligomers

L11 ANSWER 33 OF 85 USPATFULL on STN
TI Copper-catalyzed formation of carbon heteroatom and carbon-carbon
bonds

L11 ANSWER 34 OF 85 USPATFULL on STN
TI Anionic and Lewis base photopolymerization process and its use
for
making optical articles

L11 ANSWER 35 OF 85 USPATFULL on STN
TI ***Thiol*** ester compositions and processes for making and
using
same

L11 ANSWER 36 OF 85 USPATFULL on STN
TI ***Thiol*** ester compositions and processes for making and
using
same

L11 ANSWER 37 OF 85 USPATFULL on STN
TI Compositions useful as coatings, their preparation, and articles
made
therefrom

L11 ANSWER 38 OF 85 USPATFULL on STN
TI Anionic and Lewis base photopolymerization process and its use
for
making optical articles

L11 ANSWER 39 OF 85 USPATFULL on STN
TI Photocrosslinked hydrogel blend surface coatings

L11 ANSWER 40 OF 85 USPATFULL on STN
TI Dual cure reaction products of self-photoinitiating
multifunctional
acrylates with ***thiols*** and synethetic methods

L11 ANSWER 41 OF 85 USPATFULL on STN
TI Photoactivable nitrogen bases

L11 ANSWER 42 OF 85 USPATFULL on STN
TI Novel mono- and di-fluorinated beozothiepine compmunds as
inhibitors of
apical sodium co-dependent bile acid transport (ASBT) and
taurocholate
uptake

L11 ANSWER 43 OF 85 USPATFULL on STN
TI Microbial transformation method for the preparation of an
epothilone

L11 ANSWER 44 OF 85 USPATFULL on STN
TI Microbial transformation method for the preparation of an

epothilone

L11 ANSWER 45 OF 85 USPATFULL on STN
TI Derivatives of gambogic acid and analogs as activators of caspases and inducers of apoptosis

L11 ANSWER 46 OF 85 USPATFULL on STN
TI Method for anion-exchange adsorption and anion-exchangers

L11 ANSWER 47 OF 85 USPATFULL on STN
TI Novel mono- and di-fluorinated benzothiepine compounds as inhibitors of apical sodium co-dependent bile acid transport (ASBT) and taurocholate uptake

L11 ANSWER 48 OF 85 USPATFULL on STN
TI Dental polymer film

L11 ANSWER 49 OF 85 USPATFULL on STN
TI Copper-catalyzed formation of carbon-heteroatom and carbon-carbon bonds

L11 ANSWER 50 OF 85 USPATFULL on STN
TI Novel benzothiepines having activity as inhibitors of ileal bile acid transport and taurocholate uptake

L11 ANSWER 51 OF 85 USPATFULL on STN
TI Lactacystin analogs

L11 ANSWER 52 OF 85 USPATFULL on STN
TI Process for the preparation of 3,7-disubstituted-2,3,4,5-tetrahydro-1H-1,4-benzodiazepine compounds

L11 ANSWER 53 OF 85 USPATFULL on STN
TI High strength epoxy adhesive and uses thereof

L11 ANSWER 54 OF 85 USPATFULL on STN
TI Copper-catalyzed formation of carbon-heteroatom and carbon-carbon bonds

L11 ANSWER 55 OF 85 USPATFULL on STN
TI Retroviral protease inhibitors

L11 ANSWER 56 OF 85 USPATFULL on STN
TI Composition of epoxy resin, chain extender and polymeric toughener with separate base catalyst

L11 ANSWER 57 OF 85 USPATFULL on STN
TI Inhibiting discoloration of halogen-containing polymers after radiation

L11 ANSWER 58 OF 85 USPATFULL on STN
TI Thiolamide curing agents

L11 ANSWER 59 OF 85 USPATFULL on STN

TI Substituted 5-aryl-benzothiepines having activity as inhibitors of ileal bile acid transport and taurocholate uptake

L11 ANSWER 60 OF 85 USPATFULL on STN

TI Primerless substrate repair with polyepoxide and polythiol

L11 ANSWER 61 OF 85 USPATFULL on STN

TI Reacting methylene and alkene components in presence of tertiary amine reacted with ***epoxide***

L11 ANSWER 62 OF 85 USPATFULL on STN

TI Isocyanate reactive blends and internal mould release composites

L11 ANSWER 63 OF 85 USPATFULL on STN

TI Isocyanate reactive blends and internal mould release compositions

L11 ANSWER 64 OF 85 USPATFULL on STN

TI Heat-curable reaction resin mixtures and the use thereof

L11 ANSWER 65 OF 85 USPATFULL on STN

TI Thermally curable mixture containing epoxy and formamide compounds

L11 ANSWER 66 OF 85 USPATFULL on STN

TI Isocyanate reactive blends and internal mould release compositions

L11 ANSWER 67 OF 85 USPATFULL on STN

TI Decarboxylation processes using mixed metal oxide catalysts

L11 ANSWER 68 OF 85 USPATFULL on STN

TI Reaction product of olefinically unsaturated compounds with compounds containing active hydrogen, processes for their preparation and 2-component lacquers based thereon

L11 ANSWER 69 OF 85 USPATFULL on STN

TI Encapsulant compositions for use in signal transmission devices

L11 ANSWER 70 OF 85 USPATFULL on STN

TI Polyamines and a process for the production thereof

L11 ANSWER 71 OF 85 USPATFULL on STN

TI Reaction product of olefinically unsaturated compounds with compounds containing active hydrogen, processes for their preparation and 2-component lacquers based thereon HOE 85/F 036J

L11 ANSWER 72 OF 85 USPATFULL on STN

TI Tin or bismuth complex catalysts and trigger cure of coatings therewith

L11 ANSWER 73 OF 85 USPATFULL on STN

TI Rapid curing epoxy compositions

L11 ANSWER 74 OF 85 USPATFULL on STN

TI Epoxy/nucleophile transesterification catalysts and thermoset

coatings

L11 ANSWER 75 OF 85 USPATFULL on STN
TI Powder coatings with catalyzed transesterification cure

L11 ANSWER 76 OF 85 USPATFULL on STN
TI Heat-hardenable ***epoxide*** resin mixtures

L11 ANSWER 77 OF 85 USPATFULL on STN
TI Modified disulfide polymer composition and method for making same
from ***mercaptan*** terminated disulfide polymer and diethyl
formal ***mercaptan*** terminated polysulfide

L11 ANSWER 78 OF 85 USPATFULL on STN
TI Transesterification process

L11 ANSWER 79 OF 85 USPATFULL on STN
TI Polyamines and a process for their production

L11 ANSWER 80 OF 85 USPATFULL on STN
TI Process for the preparation of polyamines from N-monoaryl-N',N'-
dialkyl urea compounds and their use for the synthesis of polyurethanes

L11 ANSWER 81 OF 85 USPATFULL on STN
TI N-[2-Amino(oxy- or thia- group-substituted-
cycloaliphatic)]benzeneacetamides and -benzamide analgesics

L11 ANSWER 82 OF 85 USPATFULL on STN
TI Process for the preparation of stabilized polymer dispersions in
polyol at low temperature

L11 ANSWER 83 OF 85 USPATFULL on STN
TI Broken-down organic lignin-cellulose silicate polymers

L11 ANSWER 84 OF 85 USPATFULL on STN
TI Polyepoxide curing by polymercaptans catalyzed by dimethylamino
alkyl ethers

L11 ANSWER 85 OF 85 USPATFULL on STN
TI High resilience flexible foamed polyurethanes, foamable mixtures
and process therefor

=> d 26,31,36 hit ibib

L11 ANSWER 26 OF 85 USPATFULL on STN
TI ***Thiol*** ester compositions and processes for making and
using same
AB ***Thiol*** ester compositions, methods of making the
thiol ester compositions, and methods of using the ***thiol***
ester compositions are provided. In some embodiments, the ***thiol***

ester compositions include ***thiol*** esters, hydroxy ***thiol*** esters and cross-linked ***thiol*** esters. The ***thiol*** ester composition can be used to produce cross-linked ***thiol*** esters, sulfonic acid-containing esters, sulfonate containing esters and thioacrylate containing esters. The ***thiol*** ester compositions can be used to produce polythiourethanes. The polythiourethanes can be

used in fertilizers and fertilizer coatings.

SUMM The invention relates to ***thiol*** containing ester compositions generally made from a reaction of unsaturated ester compositions and a material capable of forming a ***thiol*** group. The invention also relates to the processes for preparing such ***thiol*** containing compositions and uses for the ***thiol*** containing compositions.

SUMM The present invention advantageously provides ***thiol*** containing compositions and methods of making such compositions.

In addition to the compositions and methods of making such compositions, products that include such compositions are also provided.

SUMM As an embodiment of the present invention, a ***thiol*** ester composition is advantageously provided. In this embodiment, the ***thiol*** ester composition includes ***thiol*** ester molecules that have an average of at least 1.5 ester groups per ***thiol*** ester molecule. The ***thiol*** ester molecules also have an average of at least 1.5 ***thiol*** groups per ***thiol*** ester molecule. The ***thiol*** ester molecules also have a molar ratio of cyclic sulfides to ***thiol*** groups of less than 1.5.

SUMM In some aspects, the ***thiol*** ester molecules have a molar ratio of cyclic sulfides to ***thiol*** groups ranging from 0 to 1.0. In some aspects, the ***thiol*** ester molecules have an average ranging from 1.5 to 9 ***thiol*** groups per ***thiol*** ester molecule. In some embodiments, the ***thiol*** ester molecules have a molar ratio of carbon-carbon double bonds to ***thiol*** groups of less than 1.5.

SUMM The amount of ***thiol*** sulfur or ***mercaptan*** sulfur contained within the ***thiol*** ester molecules can also

vary. For example, in some embodiments, the ***thiol*** ester molecules have an average of greater than 5 weight percent ***thiol*** sulfur. In other embodiments, the ***thiol*** ester molecules have an average ranging from 8 to 10 weight percent ***thiol*** sulfur. In some embodiments, the ***thiol*** ester molecules have an average of less than 30 mole percent sulfur, which is present as cyclic sulfides. Alternatively, the ***thiol*** ester molecules have an average of less than 2 mole percent sulfur present as cyclic sulfides.

SUMM In some embodiments, the ***thiol*** ester molecules are produced from unsaturated esters that have an average of less than 25 weight percent of side chains that include 3 contiguous methylene interrupted carbon-carbon double bonds. In another aspect, greater than 40 percent of the total side chains contained within the ***thiol*** ester molecules contain sulfur.

SUMM In addition to the ***thiol*** ester composition, a process for producing the ***thiol*** ester composition is advantageously provided as another embodiment of the present invention. To produce the ***thiol*** ester composition, hydrogen sulfide is contacted with an unsaturated ester composition. The unsaturated ester composition includes unsaturated esters that have an average of at least 1.5 ester groups per unsaturated ester molecule. The unsaturated esters also have an average of at least 1.5 carbon-carbon double bonds per unsaturated ester molecule. The hydrogen sulfide and the unsaturated esters are reacted to produce or form the ***thiol*** ester composition. The ***thiol*** ester composition advantageously includes ***thiol*** ester molecules that have a molar ratio of cyclic sulfides to ***thiol*** groups of less than 1.5.

SUMM Another process for producing the ***thiol*** ester composition is advantageously provided as another embodiment of the present invention.

In this process embodiment, the hydrogen sulfide and the unsaturated ester composition are contacted. The unsaturated ester composition includes unsaturated esters having an average of at least 1.5

ester groups per unsaturated ester molecule and having an average of at least 1.5 carbon-carbon double bonds per unsaturated ester molecule. The hydrogen sulfide and the unsaturated esters are then reacted in a substantial absence of a solvent to form the ***thiol*** ester composition. The ***thiol*** ester composition includes ***thiol*** ester molecules. The ***thiol*** ester composition advantageously includes ***thiol*** ester molecules that have a molar ratio of cyclic sulfides to ***thiol*** groups of less than 1.5.

SUMM The resulting ***thiol*** ester molecules produced by this process possess advantageous characteristics. For example, in some embodiments, the ***thiol*** ester molecules have a molar ratio of the hydrogen sulfide to carbon-carbon double bonds of greater than 2. As another example, in other embodiments, the ***thiol*** ester molecules have an average of greater than 5 weight percent ***thiol*** sulfur. In some aspects, greater than 40 percent of the ***thiol*** ester molecule total side chains contain sulfur.

SUMM As another embodiment of the present invention, another process for preparing the ***thiol*** ester composition is advantageously provided. In this embodiment, a polyol composition and a ***thiol*** carboxylic acid composition are contacted and reacted to produce the ***thiol*** ester composition. The ***thiol*** ester composition includes ***thiol*** ester molecules having an average of at least 1.5 ester groups per ***thiol*** ester molecule and having an average of at least 1.5 ***thiol*** groups per ***thiol*** ester molecule.

SUMM In addition to the ***thiol*** ester composition, other compositions are advantageously provided as embodiments of the present invention. For example, a hydroxy ***thiol*** ester composition is provided as another embodiment of the present invention. The hydroxyl ***thiol*** ester composition includes hydroxy ***thiol*** ester molecules having an average of at least 1.5 ester groups per hydroxy

1.5 ***thiol*** ester molecule and having an average of at least .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule.

SUMM As described herein, the .alpha.-hydroxy ***thiol*** groups contain an alcohol or hydroxy group and a ***thiol*** group within the same group. In embodiments of the present invention, the .alpha.-hydroxy ***thiol*** groups can be replaced with separate alcohol and ***thiol*** groups. In these embodiments, the same number of .alpha.-hydroxy groups can be used for the separate alcohol and ***thiol*** groups. For example, in some embodiments, the hydroxy ***thiol*** ester molecules have an average of at least 1.5 .alpha.-hydroxy ***thiol*** groups. In embodiments that contain separate alcohol and ***thiol*** groups, the hydroxy ***thiol*** ester molecules would contain an average of at least 1.5 alcohol groups and an average of at least 1.5 ***thiol*** groups.

SUMM In some aspects, the hydroxy ***thiol*** ester molecules have an average ranging from 1.5 to 9 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule. In some embodiments, the ***thiol*** ester molecules have a molar ratio of carbon-carbon double bonds to ***thiol*** groups of less than 1.5.

SUMM In some embodiments, the ***thiol*** ester molecules are produced from unsaturated esters that have an average of less than 25 weight percent of side chains that include 3 contiguous methylene interrupted carbon-carbon double bonds. In another aspect, greater than 40 percent of the total side chains contained within the .alpha.-hydroxy ***thiol*** ester molecules contain sulfur.

SUMM The amount of ***thiol*** sulfur contained within the hydroxy ***thiol*** ester molecules can also vary. For example, in some embodiments, the hydroxy ***thiol*** ester molecules have an average of greater than 5 weight percent ***thiol*** sulfur. In other embodiments, the hydroxy ***thiol*** ester molecules have an average ranging from 8 to 10 weight percent ***thiol*** sulfur.

SUMM In some embodiments, the hydroxy ***thiol*** ester molecules have a molar ratio of ***epoxide*** groups to the .alpha.-hydroxy

thiol groups of less than 2. In other aspects, the composition is substantially free of ***epoxide*** groups.

SUMM In addition to the hydroxy ***thiol*** ester composition, methods or processes for making the hydroxy ***thiol*** ester composition are advantageously provided as embodiments of the present invention. In an embodiment, a process for preparing the hydroxy ***thiol*** ester composition is provided that includes the step of contacting the hydrogen sulfide and an epoxidized unsaturated ester composition. The epoxidized unsaturated ester composition includes epoxidized unsaturated esters having an average of at least 1.5 ester groups per epoxidized unsaturated ester molecule and having an average of at least 1.5 ***epoxide*** groups per epoxidized unsaturated ester molecule. The hydrogen sulfide and the epoxidized unsaturated esters are then reacted to form the hydroxy ***thiol*** ester composition.

SUMM In some embodiments, a molar ratio of the hydrogen sulfide to ***epoxide*** groups in the epoxidized unsaturated esters is greater than 1.

SUMM Another process for preparing the hydroxy ***thiol*** ester composition is advantageously provided as another embodiment of the present invention. In this process embodiment, a polyol composition and a hydroxy ***thiol*** carboxylic acid composition are contacted and reacted to produce the hydroxy ***thiol*** ester composition. In this embodiment, the hydroxy ***thiol*** ester composition includes hydroxy ***thiol*** ester molecules having an average of at least 1.5 ester groups per hydroxy ***thiol*** ester molecule and having an average of at least 1.5 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule.

SUMM A cross-linked ***thiol*** ester composition is advantageously provided as another embodiment of the present invention. The cross-linked ***thiol*** ester composition includes ***thiol*** ester oligomers having at least two ***thiol*** ester monomers connected by a polysulfide linkage having a structure --S.sub.Q--, wherein Q is greater than 1. In some embodiments, the

thiol
ester oligomers have at least three ***thiol*** ester monomers connected by polysulfide linkages. In another aspect, the ***thiol*** ester oligomers have from 3 to 20 ***thiol*** ester monomers connected by polysulfide linkages.

SUMM In an aspect, the cross-linked ***thiol*** ester composition includes both ***thiol*** ester monomers and ***thiol*** ester oligomers. In some embodiments, the ***thiol*** ester monomers and ***thiol*** ester oligomers have a total ***thiol*** sulfur content ranging from 0.5 to 8 weight percent; or alternatively, from 8 to 15 weight percent. The combined ***thiol*** ester monomers and ***thiol*** ester oligomers can have an average molecular weight greater than 2000; or alternatively, in a range from 2000 to 20,000.

SUMM As another embodiment of the present invention, a cross-linked ***thiol*** ester composition produced by the process comprising the steps of contacting the ***thiol*** ester composition with an oxidizing agent and reacting the ***thiol*** ester and the oxidizing agent to form ***thiol*** ester oligomers is advantageously provided. In this embodiment, the ***thiol*** ester oligomers have at least two ***thiol*** ester monomers connected by a polysulfide linkage having a structure --S.sub.Q--, wherein Q is greater than 1.

SUMM A process to produce the cross-linked ***thiol*** ester composition is also advantageously provided as another embodiment of the present invention. In this process, a ***thiol*** ester composition is contacted and reacted with an oxidizing agent to form ***thiol*** ester oligomers having at least two ***thiol*** ester monomers connected by a polysulfide linkage having a structure --S.sub.Q--, wherein Q is greater than 1. In some embodiments, the oxidizing agent is elemental sulfur, oxygen, or hydrogen peroxide. In an aspect, the oxidizing agent is elemental sulfur.

SUMM In an aspect, the ***thiol*** ester is a hydroxy ***thiol*** ester. In other aspects, a weight ratio of elemental sulfur to ***thiol*** sulfur in the ***thiol*** ester molecules ranges from

0.5 to 32.

SUMM The step of the reacting the ***thiol*** ester and the oxidizing agent can be performed at a temperature ranging from 25.degree. C. to 150.degree. C. The process for producing the cross-linked ***thiol*** ester composition can also include the step of stripping residual hydrogen sulfide from the cross-linked ***thiol*** ester composition produced. In another aspect, the reaction of the ***thiol*** ester and the elemental sulfur is catalyzed. In some embodiments, the catalyst is an amine.

SUMM In another of its aspects, the present invention relates to a controlled release fertilizer material comprising a particulate plant nutrient surrounded by a coating which is the reaction product of a mixture comprising: (i) a first component selected from an isocyanate and/or an epoxy resin, and (ii) a first active hydrogen-containing compound selected from the group consisting of: a ***thiol*** ester composition; a hydroxy ***thiol*** ester composition; a cross-linked ***thiol*** ester composition and mixtures thereof.

SUMM In another of its aspects, the present invention relates to a process for the production of abrasion resistant polythiourethane and/or epoxy polymer encapsulated controlled release fertilizer particles by incorporating in urethane and/or epoxy polymer forming reaction mixture a sulfur-containing compound such as one or more of a ***thiol*** ester composition; a hydroxy ***thiol*** ester composition; a cross-linked ***thiol*** ester composition, other sulfur-based compounds described herein below and mixtures thereof.

SUMM Preferably, for the production of the present polythiourethane encapsulated controlled release fertilizer material, a sulfur-containing compound (e.g., one or more of a ***thiol*** ester composition; a hydroxy ***thiol*** ester composition; a cross-linked ***thiol*** ester composition) is used as one of the isocyanate-reactive components (alone or in combination with other active hydrogen-containing compounds). Preferably, the sulfur-containing compound comprises a sulfur-containing vegetable oil. In one preferred embodiment, the sulfur-containing vegetable oil comprises a mercaptanized

vegetable oil (MVO), more preferably as described in more detail herein, even more preferably an MVO produced by the addition of hydrogen sulfide to a vegetable oil. In another preferred embodiment, the sulfur-containing vegetable oil comprises mercapto-hydroxy vegetable oil (MHVO), more preferably as described in more detail herein, even more preferably an MHVO produced by the addition of hydrogen sulfide to epoxidized vegetable oil. In yet another preferred embodiment, the sulfur containing vegetable oil comprises sulfur cross-linked mercaptanized vegetable oil (CMVO), more preferably as described in more detail herein, even more preferably an CMVO produced by the addition of elemental sulfur to mercaptanized vegetable oil (MVO).

SUMM Preferably, for the production of epoxy polymer encapsulated controlled release fertilizer material, a sulfur-containing compound (e.g., one or more of a ***thiol*** ester composition; a hydroxy ***thiol*** ester composition; a cross-linked ***thiol*** ester composition) is used as one of the isocyanate-reactive components (alone or in combination with other active hydrogen-containing compounds). Preferably, the sulfur-containing compound comprises a sulfur-containing vegetable oil (e.g., MVO and/or MHVO and/or CMVO) is used as one of the epoxy resin-reactive components.

DRWD FIG. 1 includes two graphs that compare the NMR's of soybean oil, which is shown in the top graph, and a ***thiol*** containing ester produced from soybean oil in accordance with an embodiment of the present invention, which is shown in the bottom graph;

DRWD FIG. 2 includes two graphs that compare the NMR's of epoxidized soybean oil, which is shown in the top graph, and a ***thiol*** containing ester produced from epoxidized soybean oil in accordance with an embodiment of the present invention, which is shown in the bottom graph;

DRWD FIG. 3 is a gas chromatograph (GC)/mass spectrometer (MS) trace of a ***thiol*** containing ester that was produced from soybean oil in accordance with an embodiment of the present invention and then treated by methanolysis;

DRWD FIG. 5 is a GC/MS trace of hydroxy ***thiol*** containing ester produced from epoxidized soybean oil in accordance with an embodiment of the present invention and then treated by methanolysis;

DETD In this specification, " ***thiol*** ester composition"

refers to an ester composition that includes " ***thiol*** ester molecules." The ***thiol*** ester molecule has at least one ***thiol*** group and at least one ester group within the ***thiol*** ester molecule.

DETD In this specification, "hydroxy ***thiol*** ester composition" refers to an ester composition that includes "hydroxy ***thiol*** ester molecules." The hydroxy ***thiol*** ester molecule has at least one ***thiol*** group, at least one ester group, and at least one hydroxy or alcohol group within the hydroxy ***thiol*** ester molecule. Alternatively, the alcohol group and the ***thiol*** group can be combined in the same group, which is referred to as an ".alpha.-hydroxy ***thiol*** group."

DETD In this specification, "polythiourethane" refers to a urethane composition that includes more than one of the following structure:

#\$STR1# The presence of the thiourethane group can be determined by method known to those skilled in the art (for example infrared spectroscopy, Raman spectroscopy, and/or NMR). ***Thiol***

Ester Composition

DETD The present invention advantageously provides a ***thiol*** ester composition as an embodiment of the present invention. The ***thiol*** ester composition includes ***thiol*** ester molecules that have an average of at least 1.5 ester groups and an average of at least 1.5 ***thiol*** groups per ***thiol*** ester molecule. The ***thiol*** ester composition also has a molar ratio of cyclic sulfides to ***thiol*** groups of less than 1.5, as described herein.

DETD Generally, the ***thiol*** ester composition contains molecules having at least one ester group and at least one ***thiol*** group. The ***thiol*** ester composition of this invention can be produced from any unsaturated ester, as described herein. Because the feedstock unsaturated esters can contain multiple carbon-carbon double bonds per unsaturated ester molecule, carbon-carbon double bond reactivity and statistical probability dictate that each ***thiol*** ester molecule of the ***thiol*** ester composition produced from the unsaturated ester composition will not have the same number of ***thiol***

groups, number of unreacted carbon-carbon double bonds, number of cyclic sulfides, molar ratio of carbon-carbon double bonds to ***thiol*** groups, molar ratio of cyclic sulfides to ***thiol*** groups and other quantities of functional groups and molar ratios disclosed herein as the feedstock unsaturated ester. Additionally, the feedstock unsaturated esters can also comprise a mixture of individual unsaturated esters having a different number of carbon-carbon double bonds and/or ester groups. Thus, many of these properties will be discussed as an average number of the groups per ***thiol*** ester molecule within the ***thiol*** ester composition or average ratio per ***thiol*** ester molecule within the ***thiol*** ester composition. In other embodiments, it is desired to control the content of ***thiol*** sulfur present in the ***thiol*** ester. Because it is difficult to ensure that the hydrogen sulfide reacts with every carbon-carbon double bond within the unsaturated ester, certain molecules of ***thiol*** ester can have more or less ***thiol*** groups than other molecules. Thus, the weight percent of ***thiol*** groups is stated as an average across all ***thiol*** ester molecules of the ***thiol*** ester composition.

DETD The ***thiol*** ester can be derived from any unsaturated ester described herein.

DETD The ***thiol*** ester compositions can be described as comprising one or more separate or discreet functional groups of the ***thiol*** ester molecule and/or ***thiol*** ester composition. These independent functional groups can include: the number of (or average number of) ester groups per ***thiol*** ester molecule, ***thiol*** containing the number of (or average number of) ***thiol*** groups per ***thiol*** ester molecule, the number of (or average number of) unreacted carbon-carbon double bonds per ***thiol*** ester molecule, the average ***thiol*** sulfur content of the ***thiol*** ester composition, the percentage (or average percentage) of sulfide linkages per ***thiol*** ester molecule, and the percentage (or average percentage) of cyclic sulfide groups per ***thiol*** ester molecule. Additionally, the ***thiol***

ester compositions can be described using individual or a combination of ratios including the ratio of double bonds to ***thiol*** groups, the ratio of cyclic sulfides to ***mercaptan*** group, and the like. As separate elements, these functional groups of the ***thiol*** composition will be described separately.

DETD Minimally, in some embodiments, the ***thiol*** ester contains ***thiol*** ester molecules having at least one ester group and one ***thiol*** group per ***thiol*** ester molecule. As the ***thiol*** ester is prepared from unsaturated esters, the ***thiol*** ester can contain the same number of ester groups as the unsaturated esters described herein. In an embodiment, the ***thiol*** ester molecules have an average of at least 1.5 ester groups per ***thiol*** ester molecule. Alternatively, the ***thiol*** ester molecules have an average of at least 2 ester groups per ***thiol*** ester molecule; alternatively, an average of at least 2.5 ester groups per ***thiol*** ester molecule; or alternatively, an average of at least 3 ester groups per ***thiol*** ester molecule. In other embodiments, the ***thiol*** esters have an average of from 1.5 to 8 ester groups per ***thiol*** ester molecule; alternatively, an average of from 2 to 7 ester groups per ***thiol*** ester molecule; alternatively, an average of from 2.5 to 5 ester groups per ***thiol*** ester molecule; or alternatively, an average of from 3 to 4 ester groups per ***thiol*** ester molecule. In yet other embodiments, the ***thiol*** ester comprises an average of 3 ester groups per ***thiol*** ester molecule or alternatively, an average of 4 ester groups per unsaturated ester molecule.

DETD Minimally, the ***thiol*** ester comprises an average of at least one ***thiol*** group per ***thiol*** ester molecule. In an embodiment, the ***thiol*** ester molecules have an average of at least 1.5 ***thiol*** groups per ***thiol*** ester molecule; alternatively, ***thiol*** containing an average of at least 2 ***thiol*** groups per ***thiol*** ester molecule; alternatively, an average of at least 2.5 ***thiol*** groups per ***thiol*** ester molecule; or alternatively, an average of at least 3

thiol groups per ***thiol*** ester molecule. In other embodiments, the ***thiol*** ester molecules have an average of from 1.5 to 9 ***thiol*** groups per ***thiol*** ester molecule; alternatively, an average of from 3 to 8 ***thiol*** groups per ***thiol*** ester molecule; alternatively, ***thiol*** containing an average of from 2 to 4 ***thiol*** groups per ***thiol*** ester molecule, or alternatively, an average of from 4 to 8 ***thiol*** groups per ***thiol*** ester molecule.

DETD In other embodiments, the ***thiol*** ester can be described by the average amount of ***thiol*** sulfur present in ***thiol*** ester. In an embodiment, the ***thiol*** ester molecules have an average of at least 5 weight percent ***thiol*** sulfur per ***thiol*** ester molecule; alternatively, an average of at least 10 weight percent ***thiol*** sulfur per ***thiol*** ester molecule, or alternatively, an average of greater than 15 weight percent ***thiol*** sulfur per ***thiol*** ester molecule. In an embodiment, the ***thiol*** ester molecules have an average of from 5 to 25 weight percent ***thiol*** sulfur per ***thiol*** ester molecule; alternatively, an average of from 5 to 20 weight percent ***thiol*** sulfur per ***thiol*** ester molecule; alternatively, an average of from 6 to 15 weight percent ***thiol*** sulfur per ***thiol*** ester molecule; or alternatively, an average of from 8 to 10 weight percent ***thiol*** sulfur per ***thiol*** ester molecule.

DETD Generally, the location of the ***thiol*** group of the ***thiol*** ester is not particularly important and will be dictated by the method used to produce the ***thiol*** ester. In embodiments wherein the ***thiol*** ester is produced by contacting an unsaturated ester, the position of the ***thiol*** group will be dictated by the position of the carbon-carbon double bond. When the carbon-carbon double bond is an internal carbon-carbon double bond, the method of producing the ***thiol*** ester will result in a secondary ***thiol*** group. However, when the double bond is located at a terminal position it is possible to choose reaction conditions to produce a ***thiol*** ester comprising either a primary

DETD ***thiol*** group or a secondary ***thiol*** group. Some methods of producing the ***thiol*** ester composition can additionally create sulfur containing functional groups other than a ***thiol*** group. For example, in some ***thiol*** ester production methods, an introduced ***thiol*** group can react with a carbon-carbon double bond within the same unsaturated ester to produce a sulfide linkage. When the reaction is with a double bond of a second unsaturated ester, this produces a simple sulfide linkage. However, in some instances, the second carbon-carbon double bond is located in the same unsaturated ester molecule. When the ***thiol*** group reacts with a second carbon-carbon double bond within the same unsaturated ester molecule, a sulfide linkage is produced. In some instances, the carbon-carbon double bond can be within a second ester group of the unsaturated ester molecule. While in other instances, the carbon-carbon double bond can be within the same ester group of the unsaturated ester molecule.

DETD When the ***thiol*** group reacts with the carbon-carbon double bond in a second ester group of the same unsaturated ester molecule, the cyclic sulfide would contain two ester groups contained within a ring structure. When the ***thiol*** group reacts with the carbon-carbon double bond within the same ester group, the cyclic sulfide would not contain an ester group within the ring structure. Within this specification, this second type of cyclic sulfide is referred to as a cyclic sulfide. Within this specification, the first type of cyclic sulfide is referred to as a simple sulfide. In the cyclic sulfide case, the sulfide linkage produces a cyclic sulfide functionality within a single ester group of the ***thiol*** ester. This linkage is termed a cyclic sulfide for purposes of this application. One such sulfide group that can be produced is a cyclic sulfide. The cyclic sulfide rings that can be produced include a tetrahydrothiopyran ring, a thietane ring, or a thiophane ring (tetrahydrothiophene ring).

DETD In some embodiments, it is desirable to control the average amount of sulfur present as cyclic sulfide in the ***thiol*** ester. In

an embodiment the average amount of sulfur present as cyclic sulfide in the ***thiol*** ester molecules comprises less than 30 mole percent. Alternatively, the average amount of sulfur present as cyclic sulfide in the ***thiol*** esters comprises less than 20 mole percent; alternatively, less than 10 mole percent; alternatively, less than 5 mole percent; or alternatively, less than 2 mole percent. In other embodiments, it is desired to control the molar ratio of cyclic sulfides to ***thiol*** groups. In other embodiments, it is desirable to have molar ratios of cyclic sulfide to ***thiol*** group. In an embodiment, the average molar ratio of cyclic sulfide groups to ***thiol*** group per ***thiol*** ester is less than 1.5. Alternatively, the average molar ratio of cyclic sulfide groups to ***thiol*** group per ***thiol*** ester is less than 1; alternatively, less than 0.5; alternatively, less than 0.25; or alternatively, 0.1. In some embodiments, the ratio of cyclic sulfide groups to ***thiol*** group per ***thiol*** ester ranges from 0 to 1; or alternatively, the average molar ratio of cyclic sulfide groups to ***thiol*** group per ***thiol*** ester ranges between 0.05 and 1.

DETD In some instances it can be desirable to have carbon-carbon double bonds present in the ***thiol*** ester composition while in other embodiments it can be desirable to minimize the number of carbon-carbon double bonds present in the ***thiol*** ester composition. The presence of carbon-carbon double bonds present in the ***thiol*** ester can be stated as an average molar ratio of carbon-carbon double bonds to ***thiol*** -sulfur. In an embodiment, the average ratio of the remaining unreacted carbon-carbon double bond in the ***thiol*** ester composition to ***thiol*** sulfur is less than 1.5 per ***thiol*** ester molecule. Alternatively, the average ratio of carbon-carbon double bond to ***thiol*** sulfur is less than 1.2 per 1.2 per ***thiol*** ester molecule; alternatively, less than 1.0 per ***thiol*** ester molecule; alternatively, less than 0.75 per ***thiol*** ester molecule; alternatively, less than 0.5 per ***thiol*** ester molecule; alternatively, less than 0.2 per ***thiol*** ester molecule; or alternatively, less than 0.1 per ***thiol*** ester molecule.

DETD In particular embodiments, the ***thiol*** ester is produced

from unsaturated ester compositions. Because the feedstock unsaturated ester has particular compositions having a certain number of ester groups present, the product ***thiol*** ester composition will have about the same number of ester groups per ***thiol*** ester molecule as the feedstock unsaturated ester. Other, independent ***thiol*** ester properties described herein can be used to further describe the ***thiol*** ester composition.

DETD In some embodiments, the ***thiol*** ester molecules are produced from unsaturated esters having an average of less than 25 weight percent of side chains having 3 contiguous methylene interrupted carbon-carbon double bonds, as described herein. In some embodiments, greater than 40 percent of the ***thiol*** containing natural source total side chains can include sulfur. In some embodiments, greater than 60 percent of the ***thiol*** ester molecule total side chains can include sulfur. In other embodiments, greater than 50, 70, or 80 percent of the ***thiol*** ester molecule total side chains can include sulfur.

DETD In an embodiment, the ***thiol*** ester is a ***thiol*** containing natural source oil, as described herein. When the ***thiol*** ester is a ***thiol*** containing natural source oil, functional groups that are present in the ***thiol*** containing natural source oil can be described in a "per ***thiol*** ester molecule" basis or in a "per triglyceride" basis. The ***thiol*** containing natural source oil can have substantially the same properties as the ***thiol*** ester composition, such as the molar ratios and other independent descriptive elements described herein.

DETD The average number of ***thiol*** groups per triglyceride in the ***thiol*** containing natural source oil is greater than about 1.5. In some embodiments, the average number of ***thiol*** groups per triglyceride can range from about 1.5 to about 9.

DETD The ***thiol*** ester compositions can also be described as a product produced by the process comprising contacting hydrogen sulfide and an unsaturated ester composition and can be further limited by the process as described herein. The ***thiol*** containing

natural source oil can also be described using a molecular weight or an average molecular weight of the side chains.

DETD Hydroxy ***Thiol*** Ester Composition

DETD In embodiments of the present invention, the ***thiol*** ester compositions can also contain a hydroxy or alcohol group. When the ***thiol*** ester composition includes the hydroxy group, the ***thiol*** ester composition is referred to herein as the hydroxy ***thiol*** ester composition. The quantity or number of alcohol groups present in the hydroxy ***thiol*** ester composition can be independent of the quantity of other functional groups present in the hydroxy ***thiol*** ester composition (i.e. ***thiol*** ester groups, sulfides, cyclic sulfides). Additionally, the weight percent of ***thiol*** sulfur and functional group ratios (i.e. molar ratio of cyclic sulfides to ***thiol*** groups, molar ratio of ***epoxide*** groups to ***thiol*** groups, molar ratio of ***epoxide*** groups to .alpha.-hydroxy ***thiol*** groups and other disclosed quantities of functional groups and their molar ratios to the ***thiol*** groups) are separate or discreet elements that can be used to describe the hydroxy ***thiol*** ester composition.

The hydroxy ***thiol*** ester composition can be described using any combination of the hydroxy ***thiol*** ester composition separate functional groups or ratios described herein.

DETD In an embodiment, the hydroxy ***thiol*** ester composition is produced by reacting hydrogen sulfide with an epoxidized unsaturated ester composition as described herein. Because the epoxidized unsaturated ester can contain multiple ***epoxide*** groups, ***epoxide*** group reactivity and statistical probability dictate that not all hydroxy ***thiol*** ester molecules of the hydroxy ***thiol*** ester composition will have the same number of hydroxy groups, ***thiol*** groups, .alpha.-hydroxy ***thiol*** sulfides, cyclic sulfides, molar ratio of cyclic sulfides to ***thiol*** groups, molar ratio of ***epoxide*** groups to ***thiol*** groups, molar ratio of ***epoxide*** groups to

.alpha.-hydroxy ***thiol*** groups, weight percent ***thiol*** sulfur and other disclosed quantities of functional groups and their molar ratios as the epoxidized unsaturated ester composition. Thus, many of these properties will be discussed as an average number or ratio per hydroxy ***thiol*** ester molecule. In other embodiments, it is desired to control the content of ***thiol*** sulfur present in the hydroxy ***thiol*** ester. Because it is difficult to ensure that the hydrogen sulfide reacts with every ***epoxide*** group within the epoxidized unsaturated ester, certain hydroxy ***thiol*** ester molecules can have more or less ***thiol*** groups than other molecules within the hydroxy ***thiol*** ester composition. Thus, the weight percent of ***thiol*** groups can be stated as an average weight percent across all hydroxy ***thiol*** ester molecules. DEDT As an embodiment of the present invention, the hydroxy ***thiol*** ester composition includes hydroxy ***thiol*** ester molecules that have an average of at least 1 ester groups and an average of at least 1 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule. As an embodiment of the present invention, the hydroxy ***thiol*** ester composition includes hydroxy ***thiol*** ester molecules that have an average of at least 1.5 ester groups and an average of at least 1.5 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule. Minimally, in some embodiments, the hydroxy ***thiol*** ester comprises at least one ester, at least one ***thiol*** group, and at least one hydroxy group. Because the hydroxy ***thiol*** ester is prepared from epoxidized unsaturated esters, the hydroxy ***thiol*** ester can contain the same number of ester groups as the epoxidized unsaturated esters. In an embodiment, the hydroxy ***thiol*** ester molecules have an average of at least 1.5 ester groups per hydroxy ***thiol*** ester molecule. Alternatively, the hydroxy ***thiol*** ester molecules have an average of at least 2 ester groups per hydroxy ***thiol*** ester molecule; alternatively, an average of at

least 2.5

ester groups per hydroxy ***thiol*** ester molecule; or alternatively, an average of at least 3 ester groups per hydroxy ***thiol*** ester molecule. In other embodiments, the hydroxy ***thiol*** esters have an average of from 1.5 to 8 ester groups per hydroxy ***thiol*** ester molecule; alternatively, an average of from 2 to 7 ester groups per hydroxy ***thiol*** ester molecule; alternatively, an average of from 2.5 to 5 ester groups per hydroxy ***thiol*** ester molecule; or alternatively, an average of from 3 to 4 ester groups per hydroxy ***thiol*** ester molecule. In yet other embodiments, the .alpha.-hydroxy ***thiol*** ester comprises an average of 3 ester groups per hydroxy ***thiol*** ester molecule or alternatively, an average of 4 ester groups per hydroxy ***thiol*** ester molecule.

DETD In some embodiments, the hydroxy group and the ***thiol*** group are combined in the same group, which produces the .alpha.-hydroxy ***thiol*** group. In other embodiments, the ***thiol*** group and the hydroxy or alcohol group are not in the same group. When this occurs, to produce the hydroxy ***thiol*** ester composition, the alcohol group is added independently of the ***thiol*** group. For example, as another embodiment of the present invention, the hydroxy

thiol ester composition advantageously includes hydroxy ***thiol*** ester molecules. The hydroxy ***thiol*** ester molecules have an average of at least 1.5 ester groups, an average of at least 1.5 ***thiol*** groups, and an average of at least 1.5 alcohol

groups per hydroxy ***thiol*** ester molecule. Minimally, in some embodiments, the hydroxy ***thiol*** ester comprises at least one ***thiol*** group per hydroxy ***thiol*** ester molecule. In an embodiment, the hydroxy ***thiol*** ester molecules have an average of at least 1.5 ***thiol*** groups per hydroxy ***thiol*** ester molecule; alternatively, an average of at least 2 ***thiol*** groups per hydroxy ***thiol*** ester molecule; alternatively, an average of at least 2.5 ***thiol*** groups per hydroxy ***thiol*** ester molecule; or alternatively, an average of at least 3 ***thiol*** groups per hydroxy ***thiol***

ester molecule. In other embodiments, the hydroxy ***thiol*** ester molecules have an average of from 1.5 to 9 ***thiol*** groups per hydroxy ***thiol*** ester molecule; alternatively, an average of from 3 to 8 ***thiol*** groups per hydroxy ***thiol*** ester molecule; alternatively, an average of from 2 to 4 ***thiol*** groups per hydroxy ***thiol*** ester molecule; or alternatively, an average of from 4 to 8 ***thiol*** groups per hydroxy ***thiol*** ester.

DETD Minimally, in some embodiments, the hydroxy ***thiol*** ester composition comprises an average of at least 1 hydroxy or alcohol group per hydroxy ***thiol*** ester molecule. In some embodiments, the hydroxy ***thiol*** ester composition comprises an average of at least 1.5 hydroxy groups per hydroxy ***thiol*** ester molecule; alternatively, average of at least 2 hydroxy groups per hydroxy ***thiol*** ester molecule; alternatively, an average of at least 2.5 hydroxy groups per hydroxy ***thiol*** ester molecule; or alternatively, an average of at least 3 hydroxy groups per ***thiol*** ester molecule. In other embodiments, the ***thiol*** ester composition comprises an average of from 1.5 to 9 hydroxy groups per hydroxy ***thiol*** ester molecule; alternatively, an average of from 3 to 8 hydroxy groups per hydroxy ***thiol*** ester molecule; alternatively, an average of from 2 to 4 hydroxy groups per hydroxy ***thiol*** ester molecule; or alternatively, an average of from 4 to 8 hydroxy groups per hydroxy ***thiol*** ester molecule.

DETD In yet other embodiments, the number of hydroxy groups can be stated as an average molar ratio of hydroxy group to ***thiol*** groups. Minimally, in some embodiments, the molar ratio of hydroxy groups to ***thiol*** groups is at least 0.25. In some embodiments, the molar ratio of hydroxy groups to ***thiol*** groups is at least 0.5; alternatively, at least 0.75; alternatively, at least 1.0; alternatively, at least 1.25; or alternatively, at least 1.5. In other embodiments, the molar ratio of hydroxy groups to ***thiol*** groups ranges from 0.25 to 2.0; alternatively, from 0.5 to 1.5; or alternatively, from 0.75 to 1.25.

DETD In embodiments where the hydroxy ***thiol*** esters are

produced from an epoxidized unsaturated ester, the hydroxy ***thiol*** esters can be described as containing ester groups and .alpha.-hydroxy ***thiol*** groups. The number of ester groups and the number of .alpha.-hydroxy ***thiol*** groups are independent elements and as such the hydroxy ***thiol*** esters can be described as having any combination of ester groups and .alpha.-hydroxy ***thiol*** groups described herein. Minimally, the hydroxy ***thiol*** ester comprises an average of at least 1 .alpha.-hydroxy ***thiol*** group per hydroxy ***thiol*** ester molecule. In some embodiments, the hydroxy ***thiol*** ester composition comprises an average of at least 1.5 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule; alternatively, an average of at least 2 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule; alternatively, an average of at least 2.5 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule; or alternatively, an average of at least 3 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule. In other embodiments, the hydroxy ***thiol*** ester composition comprises an average of from 1.5 to 9 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule; alternatively, an average of from 3 to 8 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule; alternatively, an average of from 2 to 4 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule; or alternatively, an average of from 4 to 8 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule.

DETD The hydroxy ***thiol*** esters can be produced by contacting an epoxidized ester derived from an unsaturated ester (i.e., epoxidized unsaturated ester), as described herein. In some instances it can be desirable to have ***epoxide*** groups present in the hydroxy ***thiol*** ester composition. While in other embodiments, it can be desirable to minimize the number of epoxy groups present in the hydroxy ***thiol*** ester composition. Thus, the presence of residual ***epoxide*** groups can be another separate functional group used to describe the hydroxy ***thiol*** ester.

DETD The presence of ***epoxide*** groups in the hydroxy ***thiol*** ester can be independently described as an average number of ***epoxide*** groups per hydroxy ***thiol*** ester, a molar ratio of ***epoxide*** groups to ***thiol*** groups, a molar ratio of ***epoxide*** groups to .alpha.-hydroxy ***thiol*** groups, or any combination thereof. In some embodiments, the hydroxy ***thiol*** ester molecules comprise an average of less than 2 ***epoxide*** groups per hydroxy ***thiol*** ester molecule, i.e., the hydroxy ***thiol*** ester molecules have a molar ratio of ***epoxide*** groups to .alpha.-hydroxy ***thiol*** groups of less than 2. Alternatively, the hydroxy ***thiol*** ester comprises an average of less than 1.5 ***epoxide*** groups per hydroxy ***thiol*** ester molecule; alternatively, an average of less than 1 ***epoxide*** group per hydroxy ***thiol*** ester molecule; alternatively, an average of less than 0.75 ***epoxide*** groups per hydroxy ***thiol*** ester molecule; or alternatively, an average of less than 0.5 ***epoxide*** groups per hydroxy ***thiol*** ester molecule.

In other embodiments, the molar ratio of ***epoxide*** groups to ***thiol*** groups averages less than 1.5. Alternatively, the molar ratio of ***epoxide*** groups to ***thiol*** groups averages less than 1; alternatively, averages less than 0.75; alternatively, averages less than 0.5; alternatively, averages less than 0.25; or alternatively, averages less than 0.1. In yet other embodiments, the molar ratio of ***epoxide*** groups to .alpha.-hydroxy ***thiol*** groups averages less than 1.5. Alternatively, the molar ratio of ***epoxide*** groups to .alpha.-hydroxy ***thiol*** groups averages less than 1; alternatively, averages less than 0.75; alternatively, averages less than 0.5; alternatively, averages less than 0.25; or alternatively, averages less than 0.1.

DETD In some embodiments, the hydroxy ***thiol*** ester composition is substantially free of ***epoxide*** groups.

DETD In other embodiments, the hydroxy ***thiol*** ester can be described by the average amount of ***thiol*** sulfur present in hydroxy ***thiol*** ester. In an embodiment, the hydroxy ***thiol*** ester molecules have an average of at least 2.5

weight percent ***thiol*** sulfur per hydroxy ***thiol*** ester molecule; alternatively, an average of at least 5 weight percent ***thiol*** sulfur per hydroxy ***thiol*** ester molecule; alternatively, an average of at least 10 weight percent ***thiol*** sulfur per hydroxy ***thiol*** ester molecule; or alternatively, an average of greater than 15 weight percent ***thiol*** sulfur per hydroxy ***thiol*** ester molecule. In an embodiment, the hydroxy ***thiol*** ester molecules have an average of from 5 to 25 weight percent percent ***thiol*** sulfur per hydroxy ***thiol*** ester molecule; alternatively, an average of from 5 to 20 weight percent ***thiol*** sulfur per hydroxy ***thiol*** ester molecule; or alternatively, an average of from 6 to 15 weight percent ***thiol*** sulfur per hydroxy ***thiol*** ester molecule; or alternatively, an average of from 8 to 10 weight percent ***thiol*** sulfur per hydroxy ***thiol*** ester molecule.

DETD In some embodiments, at least 20 percent of the total side chains include the .alpha.-hydroxy ***thiol*** group. In some embodiments, at least 20 percent of the total side chains include the .alpha.-hydroxy ***thiol*** group. In some embodiments, at least 60 percent of the total side chains include the .alpha.-hydroxy ***thiol*** group; alternatively, at least 70 percent of the total side chains include the .alpha.-hydroxy ***thiol*** group. Yet in other embodiments, at least 80 percent of the total side chains include the .alpha.-hydroxy ***thiol*** group.

DETD In some aspects, greater than 20 percent of the hydroxy ***thiol*** ester molecule total side chains contain sulfur. In some aspects, greater than 40 percent of the hydroxy ***thiol*** ester molecule total side chains contain sulfur. In some aspects, greater than 60 percent of the hydroxy ***thiol*** ester molecule total side chains contain sulfur; alternatively, greater than 70 percent of the total side chains contain sulfur; or alternatively, greater than 80 percent of the total side chains contain sulfur.

DETD In particular embodiments, the epoxidized unsaturated ester used in the synthesis of the hydroxy ***thiol*** ester is produced from

the epoxidized unsaturated ester composition that includes an epoxidized natural source oil. Because the natural source oils have particular compositions regarding the number of ester groups present, the hydroxy ***thiol*** ester will have about the same number of ester groups as the feedstock natural source oil. Other independent properties that are described herein can be used to further describe the hydroxy ***thiol*** ester.

DETD In other embodiments, the epoxidized unsaturated ester used to produce the hydroxy ***thiol*** ester is produced from synthetic (or semi-synthetic) unsaturated ester oils. Because the synthetic ester oils can have particular compositions regarding the number of ester groups present, the hydroxy ***thiol*** ester would have about the same number of ester groups as the synthetic ester oil. Other, independent properties of the unsaturated ester, whether the unsaturated ester includes natural source or synthetic oils, can be used to further describe the hydroxy ***thiol*** ester composition.

DETD The hydroxy ***thiol*** ester compositions can also be described as a product produced by the process comprising contacting hydrogen sulfide and an epoxidized unsaturated ester composition and can be further limited by the process as described herein. The hydroxy ***thiol*** containing natural source oil can also be described using an average molecular weight or an average molecular weight of the side chains.

DETD Cross-Linked ***Thiol*** Ester Compositions

DETD In an aspect, the present invention relates to a cross-linked ***thiol*** ester composition. Generally, the cross-linked ***thiol*** ester molecules are oligomers of ***thiol*** esters that are connected together by polysulfide linkages --S.sub.x-- wherein x is an integer greater 1. As the cross-linked ***thiol*** ester is described as an oligomer of ***thiol*** esters, the ***thiol*** esters can be described as the monomer from which the cross-linked ***thiol*** esters are produced.

DETD In an aspect, the cross-linked ***thiol*** ester composition comprises a ***thiol*** ester oligomer having at least two ***thiol*** ester monomers connected by a polysulfide linkage having a structure --S.sub.Q--, wherein Q is an integer greater than 1. In an

aspect, the polysulfide linkage may be the polysulfide linkage --S.sub.Q--, wherein Q is 2, 3, 4, or mixtures thereof. In other embodiments, Q can be 2; alternatively, 3; or alternatively, 4.

DETD In an aspect, the cross-linked ***thiol*** ester composition comprises a ***thiol*** ester oligomer having at least 3 ***thiol*** ester monomers connected by polysulfide linkages; alternatively, 5 ***thiol*** ester monomers connected by polysulfide linkages; alternatively, 7 ***thiol*** ester monomers connected by polysulfide linkages; or alternatively, 10 ***thiol*** ester monomers connected by polysulfide linkages. In yet other embodiments, the cross-linked ***thiol*** ester composition comprises a ***thiol*** ester oligomer having from 3 to 20 ***thiol*** ester monomers connected by polysulfide linkages; alternatively, from 5 to 15 ***thiol*** ester monomers connected by polysulfide linkages; or alternatively, from 7 to 12 ***thiol*** ester monomers connected by polysulfide linkages.

DETD In an aspect, the cross-linked ***thiol*** ester composition comprises ***thiol*** ester monomers and ***thiol*** ester oligomers. In some embodiments, the cross-linked ***thiol*** ester composition has a combined ***thiol*** ester monomer and ***thiol*** ester oligomer average molecular weight greater than 2,000. In other embodiments, the cross-linked ***thiol*** ester composition has a combined ***thiol*** ester monomer and ***thiol*** ester oligomer average molecular weight greater than 5,000; or alternatively, greater than 10,000. In yet other embodiments, the cross-linked ***thiol*** ester composition has a combined ***thiol*** ester monomer and ***thiol*** ester oligomer average molecular weight ranging from 2,000 to 20,000; alternatively, from 3,000 to 15,000; or alternatively, from 7,500 to 12,500.

DETD In an aspect, the ***thiol*** ester monomers and ***thiol*** ester oligomers have a total ***thiol*** sulfur content greater than 0.5. In other embodiments, the ***thiol*** ester monomers and ***thiol*** ester oligomers have a total ***thiol*** sulfur content greater than 1; alternatively, greater than 2; alternatively, greater than 4. In yet other embodiments, the ***thiol*** ester monomers and the ***thiol*** ester oligomers have a total ***thiol*** sulfur content from 0.5 to 8; alternatively, from 4 to 8; or alternatively, 0.5 to 4.

DETD In an aspect, the ***thiol*** ester monomers and

thiol

ester oligomers have a total sulfur content greater than 8. In some embodiments, the ***thiol*** ester monomers and ***thiol*** ester oligomers have a total sulfur content greater than 10; alternatively, greater than 12. In yet other embodiments, the ***thiol*** ester monomers and ***thiol*** ester

oligomers have a total sulfur content ranging from 8 to 15 weight percent; alternatively,

from 9 to 14; or alternatively, from 10 to 13.

DETD The cross-linked ***thiol*** ester compositions can also be described as a product produced by the process comprising contacting a

thiol ester with oxidizing agent and can be further limited by

the process as described herein.

DETD The present invention advantageously includes sulfide-containing ester compositions as embodiments of the present invention. Generally, the

sulfide-containing ester compositions can be described as containing molecules having at least one ester group and a least one sulfide group

within each molecule. The sulfide-containing esters used in the present invention can be produced by contacting either an unsaturated ester or

an epoxidized unsaturated ester with a ***thiol*** containing compound as described herein.

DETD The feedstock unsaturated esters can contain multiple carbon-carbon double bonds per unsaturated ester molecule. The carbon-carbon double

bond reactivity and statistical probability, however, dictate that each

sulfide-containing ester molecule of the ***thiol*** - containing ester composition produced from the unsaturated ester composition will

not have the same number of sulfide groups, number of unreacted carbon-carbon double bonds, molar ratio of carbon-carbon double bonds to

sulfide groups, molar ratio of cyclic sulfides to ***thiol*** groups and other herein disclosed quantities of functional groups and molar

ratios. Additionally, the feedstock unsaturated esters can also comprise a mixture of individual unsaturated esters having a different number of

carbon-carbon double bonds and/or ester groups. Many of these properties

are discussed herein as an average number of the groups per sulfide-containing ester molecule within the sulfide-containing ester

composition or average ratio per ***thiol*** -containing ester molecule within the sulfide-containing ester composition.

DETD In embodiments related to the sulfide-containing ester that is

produced

from an epoxidized unsaturated ester, the feedstock epoxidized unsaturated esters can contain multiple ***epoxide*** groups per unsaturated ester molecule. Individual ***epoxide*** group reactivity and statistical probability dictate that each sulfide-containing ester molecule of the sulfide-containing ester composition produced from the unsaturated ester composition will not have the same number of sulfide groups, number of unreacted ***epoxide*** groups, molar ratio of ***epoxide*** groups to sulfide groups, and other herein disclosed quantities of functional groups and molar ratios. Additionally, the feedstock epoxidized unsaturated esters can also comprise a mixture of individual epoxidized unsaturated ester molecules having a different number of ***epoxide*** groups and/or ester groups. Thus, many of these properties are described as an average number of the groups per sulfide-containing ester molecules within the sulfide-containing ester composition or average ratio per ***thiol*** -containing ester molecule within the sulfide-containing ester composition.

DETD Minimally, in some embodiments, the sulfide-containing esters comprise at least one ester group per sulfide-containing ester molecule. In some embodiments, the sulfide-containing ester has an average of at least 1.5 ester groups per sulfide-containing ester molecule. Alternatively, the sulfide-containing ester molecules have an average of at least 2 ester groups per sulfide-containing ester molecule; alternatively, an average of at least 2.5 ester groups per sulfide-containing ester molecule; or alternatively, an average of at least 3 ester groups per sulfide-containing ester molecule. In other embodiments, the sulfide-containing esters have an average of from 1.5 to 9 ester groups per sulfide-containing ester molecule; alternatively, an average of from 1.5 to 8 ester groups per sulfide-containing ester molecule; alternatively, an average of from 2 to 8 ester groups per sulfide-containing ester molecule; alternatively, an average of from 2 to 7 ester groups per sulfide-containing ester molecule; alternatively, an average of from 2.5 to 5 ester groups per sulfide-containing ester molecule; alternatively, an average of from 3 to 5 ester groups per sulfide-containing ester molecule; or alternatively, an average of from 3 to 4 ester groups per sulfide-containing ester molecule. In yet other

embodiments, the hydroxy ***thiol*** -containing ester comprises an average of about 3 ester groups per sulfide-containing ester molecule; or alternatively, an average of about 4 ester groups per sulfide-containing ester molecule.

DETD In some embodiments, R.sup.3 comprises at least one functional group.

In one aspect, the functional group is selected from the group consisting of a hydroxy group, a carboxylic acid group, a carboxylic ester group, an amine group, a sulfide group, and a second ***thiol*** group. In some aspects, R.sup.3 comprises at least two functional groups. In some aspects, the functional groups are selected from the group consisting of a hydroxy group, carboxylic acid group, a carboxylic ester group, an amine group, a sulfide group, a second ***thiol*** group, and mixtures thereof.

DETD The sulfide-containing ester compositions can also be described as a

product produced by the process comprising contacting an unsaturated ester with a ***mercaptan*** and can be further limited by the

process as described herein. In other embodiments, the sulfide-containing ester composition can also be described as a product

produced by a process comprising contacting an epoxidized unsaturated ester with a ***mercaptan*** and can be further limited by the

process as described herein. Generally, the thioacrylate ester composition can be described as comprising thioacrylate molecules having at least one ester group in addition to any acrylate or thioacrylate ester groups present in the thioacrylate molecule and at least one thioacrylate group. The ester group(s) that are in addition to any acrylate or thioacrylate ester

groups present in the thioacrylate molecule are hereinafter referred to as "supplementary ester group(s)." The thioacrylate ester composition

described herein can be produced by contacting an acrylate composition with a ***thiol*** -containing ester composition and/or a hydroxy

thiol -containing ester composition, both of which are described herein.

DETD The feedstock ***thiol*** ester compositions and/or hydroxy ***thiol*** ester compositions can comprise a mixture of molecules

that have an average quantity of ester groups, ***thiol***

groups, hydroxy groups, and other groups and molar ratios described herein. Additionally, individual ***thiol*** and hydroxy group reactivity within the ***thiol*** -containing ester compositions and/or hydroxy ***thiol*** ester compositions and statistical probability dictate that each thioacrylate ester molecule of the thioacrylate ester composition produced may not have the same number of ester groups, thioacrylate groups, acrylate groups, and other herein disclosed quantities of functional groups, moieties, and molar ratios. Thus, many of the properties of the thioacrylate ester molecules within the thioacrylate ester composition are described as using an average number of the groups per thioacrylate ester molecule within the thioacrylate ester composition or as an average ratio per thioacrylate ester molecule within the thioacrylate ester composition.

DETD The thioacrylate ester can also be described as a product produced by the process that includes contacting a ***thiol*** -containing ester composition with an acrylate composition and can be further limited by the process described herein. In other embodiments, the thioacrylate ester composition can also be described as a product produced by a process that includes contacting a hydroxy ***thiol*** -containing ester composition with an acrylate composition and can be further limited by the process described herein.

DETD The present invention advantageously provides a sulfonic acid-containing ester as an embodiment of the present invention. Generally, the sulfonic acid-containing ester of the present invention includes sulfonic acid-containing ester molecules having at least one ester group and a least one sulfonic acid group. The sulfonic acid-containing ester described herein can be produced by contacting a ***thiol*** ester with an oxidizing agent as described herein. Because the feedstock for the production of the sulfonic acid-containing ester can include multiple ***thiols*** groups, ***thiol*** group reactivity and statistical probability dictate that each sulfonic acid-containing ester molecule of the sulfonic acid-containing ester will not have the same number of sulfonic acid groups. Additionally, the feedstock ***thiol*** ester can also include a mixture of individual ***thiol*** ester molecules having different numbers of

thiol

groups and/or ester groups. Thus, many of the groups present in the sulfonic acid-containing ester are described herein as an average number of the groups per sulfonic acid-containing ester molecule or an average ratio per sulfonic acid-containing ester molecule within the sulfonic acid-containing ester.

DETD In some embodiments of the present invention, the sulfonic acid ester

is substantially free of ***thiol*** groups.

DETD The sulfonic acid-containing ester can also be described as a product

produced by the process comprising contacting a ***thiol*** ester

with an oxidizing agent described herein.

DETD Process for Making a ***Thiol*** Ester Composition

DETD The present invention advantageously provides processes for producing a

thiol ester composition as embodiments of the present invention.

As an embodiment, the present invention advantageously includes a process to produce a ***thiol*** ester composition by contacting

hydrogen sulfide and an unsaturated ester composition containing unsaturated esters and reacting the hydrogen sulfide and unsaturated

esters to form or produce the ***thiol*** ester composition.

As another embodiment of the present invention, a process to produce the

thiol ester composition is advantageously provided. In this

embodiment, the process includes contacting a composition comprising a

polyol with a composition comprising a ***thiol*** containing carboxylic acid composition and reacting the polyol and

thiol containing carboxylic acid composition to form the ***thiol*** ester

composition.

DETD In some embodiments of the present invention that include producing

thiol ester compositions, the unsaturated ester composition is a natural source oil. In an aspect, the unsaturated ester

composition is soybean oil or alternatively castor oil. Other suitable types of unsaturated ester compositions are described herein and can be used in

the processes for producing the ***thiol*** ester compositions.

DETD ***Thiol*** Esters from Unsaturated Esters

DETD As an embodiment of the present invention, the ***thiol*** esters

described herein can be produced by a process comprising contacting

hydrogen sulfide and an unsaturated ester composition and

reacting

hydrogen sulfide and the unsaturated ester composition to form the ***thiol*** ester composition. In one embodiment, the unsaturated ester composition includes unsaturated esters having an average of at least 1.5 ester groups and an average of at least 1.5 carbon-carbon double bonds per unsaturated ester molecule. In this embodiment, the ***thiol*** ester composition includes ***thiol*** ester molecules having a molar ratio of cyclic sulfides to ***thiol*** groups of less than 1.5.

DETD The processes for producing the ***thiol*** ester composition can be applied to any of the unsaturated esters described herein and used to produce any of the ***thiol*** esters described herein. The process

for producing the ***thiol*** ester composition can also include any additional process steps or process conditions described herein.

DETD The hydrogen sulfide to molar equivalents of unsaturated ester carbon-carbon double bonds molar ratio utilized in the process to produce the ***thiol*** ester composition can be any molar ratio

that produces the desired ***thiol*** ester. The molar equivalents of unsaturated ester carbon-carbon double bonds is calculated by the

equation: ##EQU1## In this equation, UES GMW is the average gram

molecular weight of the unsaturated ester, UES Mass is the mass of the feedstock unsaturated ester, and UES C.dbd.C is the average number of

double bonds per unsaturated ester molecule. In some embodiments, the ***thiol*** ester molecules have a molar ratio of the hydrogen sulfide

to the unsaturated ester carbon-carbon double bonds of greater than 2.

In other embodiments, the hydrogen sulfide to unsaturated ester carbon-carbon double bonds molar ratio is greater than 5; alternatively,

greater than 10; alternatively, greater than 15; or

alternatively, greater than 20. In other embodiments, the hydrogen sulfide to unsaturated ester carbon-carbon double bonds molar ratio can be from 2 to 500; alternatively, from 5 to 200; alternatively, from 10 to 100; or

alternatively, from 100 to 200.

DETD When a continuous reactor is used, a feed unsaturated ester weight hourly space velocity ranging from 0.1 to 5 can be used to produce the

desired ***thiol*** ester. Alternatively, the feed unsaturated ester weight hourly space velocity ranges between 0.1 to 5; alternatively, from 0.1 to 2. Alternatively, the feed unsaturated ester weight hourly space velocity is 0.1; alternatively, the feed unsaturated ester weight hourly space velocity is 0.25; or alternatively, the feed unsaturated ester weight hourly space velocity is 2.

DETD The time required for the reaction of the unsaturated ester and hydrogen sulfide can be any time required to form the described ***thiol*** ester. Generally, the time required for the reaction of

the unsaturated ester and hydrogen sulfide is at least 5 minutes.

In some embodiments, the time required for the reaction of the unsaturated ester and hydrogen sulfide ranges from 5 minutes to 72 hours; alternatively, from 10 minutes to 48 hours; or alternatively, from 15

minutes to 36 hours.

DETD In embodiments, the process to produce the ***thiol*** ester further comprises a step to remove excess or residual hydrogen sulfide

after reacting the hydrogen sulfide and the unsaturated ester composition. In some embodiments, the ***thiol*** ester is

vacuum stripped. In some embodiments, the ***thiol*** ester is vacuum stripped at a temperature ranging between 25.degree. C. and 250.degree.

C.; or alternatively, between 50.degree. C. and 200.degree. C. In other

embodiments, the ***thiol*** ester is sparged with an inert gas to remove hydrogen sulfide. In some embodiments, the ***thiol*** ester is sparged with an inert gas at a temperature between 25.degree.

C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree.

C. In some aspects, the inert gas is nitrogen. Generally, the stripped

or sparged ***thiol*** ester comprises less than 0.1 weight percent

hydrogen sulfide. In other embodiments, the stripped or sparged ***thiol*** ester comprises less than 0.05 weight percent

sulfur; alternatively, less than 0.025 weight percent hydrogen sulfide;

or alternatively, less than 0.01 weight percent hydrogen sulfide

DETD The reaction between the unsaturated ester and hydrogen sulfide can be

performed at any temperature capable of forming the ***thiol*** ester. In some embodiments, the unsaturated ester and hydrogen sulfide

can be reacted at a temperature greater than -20.degree. C. In other

embodiments, the unsaturated ester and hydrogen sulfide can be reacted at a temperature greater than 0.degree. C.; alternatively, greater than 20.degree. C.; alternatively, greater than 50.degree. C.; alternatively, greater than 80.degree. C.; or alternatively, greater than 100.degree.

C. In yet other embodiments, the unsaturated ester and hydrogen sulfide can be reacted at a temperature from -20.degree. C. to 200.degree. C.; alternatively, from 120.degree. C. to 240.degree. C.; alternatively, from 170.degree. C. to 210.degree. C.; alternatively, from 185.degree. C. to 195.degree. C.; alternatively, from 20.degree. C. to 200.degree. C.; alternatively, from 20.degree. C. to 170.degree. C.; or alternatively, from 80.degree. C. to 140.degree. C.

DETD ***Thiol*** esters having a low cyclic sulfide content can be produced using the disclosed process. In an aspect, the process for producing the ***thiol*** ester forms or produces a ***thiol*** ester having a molar ratio of cyclic sulfide to ***thiol*** groups of less than 1.5. Additional cyclic sulfide to ***thiol*** groups molar ratios are disclosed herein.

DETD In addition to lower cyclic sulfide content, ***thiol*** esters having a low carbon-carbon double bond to ***thiol*** group molar ratio can also be produced using the disclosed process. In an aspect, the process described herein produces the ***thiol*** ester having a carbon-carbon double bond to ***thiol*** group molar ratio of less than 1.5. Additional carbon-carbon double bond to ***thiol*** group molar ratios are disclosed herein.

DETD In some aspects, the process described herein produces the ***thiol*** ester molecules having an average of greater than 5 weight percent ***thiol*** sulfur. Additional ***thiol*** sulfur contents are disclosed herein. In other aspects, the process for producing a ***thiol*** ester forms a ***thiol*** ester having greater than 40 percent of the ***thiol*** ester total side chains include sulfur. Other percentages of the ***thiol*** ester total side chains that include sulfur are disclosed herein.

DETD In some embodiments, the process for producing a ***thiol*** ester composition includes contacting an unsaturated ester and hydrogen sulfide and reacting the unsaturated ester and the hydrogen

sulfide to form a ***thiol*** ester. The ***thiol*** ester comprises ***thiol*** ester molecules that have a ratio of cyclic sulfide to ***thiol*** groups of less than 1.5.

DETD ***Thiol*** Ester from a Polyol and a ***Thiol*** Containing Carboxylic Acid Derivative

DETD As another embodiment of the present invention, another process to produce the ***thiol*** ester composition is advantageously provided. In this embodiment, the process includes the steps of contacting a composition comprising a polyol with a composition comprising a ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative and reacting the polyol and ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative to produce the ***thiol*** ester composition. This process can be applied to any polyol, ***thiol*** containing carboxylic acid, or ***thiol*** containing carboxylic acid derivative described herein. The process for producing the ***thiol*** ester composition can also include any additional process steps or process conditions described herein. Additionally, the process for producing the ***thiol*** ester composition can form any ***thiol*** ester described herein.

DETD In some embodiments, the ***thiol*** ester composition includes ***thiol*** ester molecules that have an average of at least 1.5 ester groups and an average of at least 1.5 ***thiol*** groups per ***thiol*** ester molecule.

DETD The polyol used to produce the ***thiol*** ester by contacting a polyol and a ***thiol*** carboxylic acid and/or ***thiol*** carboxylic acid equivalent (for example a ***thiol*** carboxylic acid methyl ester) can be any polyol or mixture of polyols that can produce the described ***thiol*** containing ester.

DETD In one aspect, the polyol used to produce the ***thiol*** ester can comprise from 2 to 20 carbon atoms. In other embodiments, the polyol comprises from 2 to 10 carbon atoms; alternatively from 2 to 7 carbon atoms; alternatively from 2 to 5 carbon atoms. In further embodiments, the polyol may be a mixture of polyols having an average of 2 to 20 carbon atoms; alternatively, an average of from 2 to 10 carbon atoms; alternatively, an average of 2 to 7 carbon atoms; alternatively an average of 2 to 5 carbon atoms.

DETD In another aspect, the polyol used to produce the ***thiol***

ester can have any number of hydroxy groups needed to produce the ***thiol*** ester as described herein. In some embodiments, the polyol has 2 hydroxy groups; alternatively 3 hydroxy groups; alternatively, 4 hydroxy groups; alternatively, 5 hydroxy groups; or alternatively, 6 hydroxy groups. In other embodiments, the polyol comprises at least 2 hydroxy groups; alternatively at least 3 hydroxy groups; alternatively, at least 4 hydroxy groups; or alternatively, at least 5 hydroxy groups; at least 6 hydroxy groups. In yet other embodiments, the polyol comprises from 2 to 8 hydroxy groups; alternatively, from 2 to 4 hydroxy groups; or alternatively from 4 to 8 hydroxy groups.

DETD In further aspects, the polyol used to produce the ***thiol*** ester is a mixture of polyols. In an embodiment, the mixture of polyols has an average of at least 1.5 hydroxy groups per polyol molecule. In other embodiments, the mixture of polyols has an average of at least 2 hydroxy groups per polyol molecule; alternatively, an average of at least 2.5 hydroxy groups per polyol molecule; alternatively, an average of at least 3.0 hydroxy groups per polyol molecule; or alternatively, an average of at least 4 hydroxy groups per polyol molecule. In yet another embodiment, the mixture of polyols has an average of 1.5 to 8 hydroxy groups per polyol molecule; alternatively, an average of 2 to 6 hydroxy groups per polyol molecule; alternatively, an average of 2.5 to 5 hydroxy groups per polyol molecule; alternatively, an average of 3 to 4 hydroxy groups per polyol molecule; alternatively, an average of 2.5 to 3.5 hydroxy groups per polyol molecule; or alternatively, an average of 2.5 to 4.5 hydroxy groups per polyol molecule.

DETD In yet another aspect, the polyol or mixture of polyols used to produce the ***thiol*** ester has a molecular weight or average molecular weight less than 500. In other embodiments, the polyol or mixture of polyols have a molecular weight or average molecular weight less than 300; alternatively less than 200; alternatively, less than 150; or alternatively, less than 100.

DETD The ***thiol*** carboxylic acid and/or ***thiol*** carboxylic acid equivalent used to produce the ***thiol*** ester by contacting

a polyol and a ***thiol*** carboxylic acid and/or ***thiol*** carboxylic acid equivalent can be any ***thiol*** carboxylic acid mixture comprising ***thiol*** carboxylic acids, ***thiol*** carboxylic acid equivalent or mixture comprising ***thiol*** carboxylic acid equivalents that can produce the described ***thiol*** containing ester. When talking about the characteristics ***thiol*** carboxylic acid equivalent or ***thiol*** carboxylic acid equivalents, properties such as number of carbon atoms, average number of carbon atom, molecular weight or average molecular weight, number of ***thiol*** group, and average number of ***thiol*** groups, one will understand the these properties will apply to the portion of the ***thiol*** carboxylic acid equivalent which adds to the polyol to form the ***thiol*** ester.

DETD In an aspect, the ***thiol*** carboxylic acid and/or ***thiol*** carboxylic acid equivalent used to produce the ***thiol*** ester comprises from 2 to 28 carbon atoms. In an embodiment, the ***thiol*** carboxylic acid and/or ***thiol*** carboxylic acid equivalent comprises from 4 to 26 carbon atoms; alternatively, from 8 to 24 carbon atoms; alternatively, from 12 to 24 carbon atoms; or alternatively, from 14 to 20 carbon atoms. In other embodiments, a mixture comprising ***thiol*** carboxylic acid and/or mixture comprising ***thiol*** carboxylic acid equivalents has an average of 2 to 28 carbon atoms per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 4 to 26 carbon atoms per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 8 to 24 carbon atoms per carboxylic acid and/or carboxylic acid equivalent; or alternatively, from 14 to 20 carbon atoms per carboxylic acid and/or carboxylic acid equivalent.

DETD In another aspect, the ***thiol*** carboxylic acid and/or ***thiol*** carboxylic acid equivalent used to produce the ***thiol*** ester has at least 1 ***thiol*** group; alternatively 2 ***thiol*** groups. In some embodiments, a mixture comprising ***thiol*** carboxylic acid and/or mixture comprising ***thiol*** carboxylic acid equivalents has an average of from 0.5 to 3 ***thiol*** groups per carboxylic acid and/or carboxylic acid

equivalent; alternatively, an average of from 1 to 2
thiol
groups per carboxylic acid and/or carboxylic acid equivalent.
DETD In another aspect, the ***thiol*** carboxylic acid and/or
thiol carboxylic acid equivalent used to produce the
thiol ester has a molecular weight greater than 100;
alternatively greater than 180; alternatively greater than 240;
or
alternatively greater than 260. In other embodiments, the
thiol
carboxylic acid and/or ***thiol*** carboxylic acid equivalent
has a
molecular weight from 100 to 500; alternatively, from 120 to 420;
alternatively, from 180 to 420; alternatively, from 240 to 420; a
mixture or alternatively, from 260 to 360. In some embodiments, a
mixture comprising ***thiol*** carboxylic acid and/or mixture
comprising ***thiol*** carboxylic acid equivalents has an
average
molecular weight greater than 100 per carboxylic acid and/or
carboxylic
acid equivalent; alternatively greater than 180 per carboxylic
acid
and/or carboxylic acid equivalent; alternatively greater than 240
per
carboxylic acid and/or carboxylic acid equivalent; or
alternatively
greater than 260 per carboxylic acid and/or carboxylic acid
equivalent.
In yet other embodiments, the mixture comprising of ***thiol***
carboxylic acid and/or mixture comprising ***thiol***
carboxylic
acid equivalents has an average molecular weight from 100 to 500
per
carboxylic acid and/or carboxylic acid equivalent; alternatively,
from
120 to 420 per carboxylic acid and/or carboxylic acid equivalent;
alternatively, from 180 to 420 per carboxylic acid and/or
carboxylic
acid equivalent; alternatively, from 240 to 420 per carboxylic
acid
and/or carboxylic acid equivalent; a mixture or alternatively,
from 260
to 360 per carboxylic acid and/or carboxylic acid equivalent.
DETD In some aspects, the reaction between the polyol and the
thiol
containing carboxylic acid and/or ***thiol*** containing
carboxylic
acid derivative occurs in the presence of a solvent. In other
aspects
the reaction between the polyol and the ***thiol***
containing
carboxylic acid and/or ***thiol*** containing carboxylic acid
derivative occurs in the substantial absence of a solvent. In
aspects
wherein the reaction between the polyol and the ***thiol***
containing carboxylic acid and/or ***thiol*** containing
carboxylic
acid derivative occurs in the presence of a solvent, the solvent
is
selected from the group consisting of an aliphatic hydrocarbon,

an ether, an aromatic compound, or any combination thereof. Generally, the solvent, regardless of its chemical class, can include from 1 to 20 carbon atoms; or alternatively, from 3 to 10 carbon atoms. When the solvent includes the aliphatic hydrocarbon, the aliphatic hydrocarbon is butane, isobutane, pentane, hexane, heptane, octane, or any mixture thereof. When the solvent includes the aromatic compound, the aromatic compound is benzene, toluene, xylene, ethylbenzene, or any mixture thereof. When the solvent includes the ether, the ether is diethyl ether, dipropyl ether, tetrahydrofuran, and any mixture thereof. DETD When a solvent is used for the reaction between the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative, the quantity of solvent can be any amount that facilitates the reaction. In some embodiments, the mass of the solvent is less than 30 times the mass of the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative. In other embodiments, the mass of the solvent is less than 20 times the mass of the unsaturated ester oil; alternatively, less than 15 times the mass of the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative; alternatively, less than 10 times the mass of the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative; or alternatively, less than 5 times the mass of the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative. In other embodiments, the mass of the solvent is from 2 times to 20 times the mass of the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative; alternatively, from 3 times to 15 times the mass of the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative; or alternatively, from 5 times to 10 times the mass of the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative. DETD The equivalent of ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative carboxylic acid

groups to equivalents of polyol hydroxy groups molar ratio (hereinafter "carboxylic acid group to polyol hydroxy group molar ratio") utilized in the process to produce the ***thiol*** ester composition can be any carboxylic acid group to polyol hydroxy group molar ratio that produces the desired ***thiol*** ester composition. In some embodiments, the carboxylic acid group to polyol hydroxy group molar ratio is greater than 0.4. In other embodiments, the carboxylic acid group to polyol hydroxy group molar ratio is greater than 0.6; alternatively, greater than 0.8; alternatively, greater than 1; or alternatively, greater than 1.1. In other embodiments, the carboxylic acid group to polyol hydroxy group molar ratio can range from 0.4 to 1.3; alternatively, from 0.6 to 1.2, or alternatively, from 0.8 to 1.1.

DETD In some aspects, the reaction between the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative is catalyzed. In some embodiments, the catalyst is a mineral acid, such as sulfuric or phosphoric acid. In other embodiments, the catalyst is an organic acid. In embodiments, for example, the organic acid is methane sulfonic acid or toluene sulfonic acid.

Other suitable types of catalyst will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD The reaction of the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative can occur in a batch reactor or a continuous reactor, as described herein. The reaction between the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative can be performed at any temperature capable of forming the ***thiol*** ester. In some embodiments, the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative can be reacted at a temperature greater than 20.degree. C. In other embodiments, the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative can be reacted at a temperature greater than 50.degree. C.; alternatively, greater than 75.degree. C.;

or alternatively, greater than 100.degree. C. In yet other embodiments, the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative can be reacted at a temperature from 20.degree. C. to 250.degree. C.; alternatively, from 50.degree. C. to 200.degree. C.; alternatively, from 75.degree. C. to 175.degree. C.; or alternatively, from 100.degree. C. to 150.degree. C.

DETD The time required for the reaction of the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative can be any time required to form the described ***thiol*** ester oil. Generally, the reaction time of the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative is at least 5 minutes. In some embodiments, the reaction time is at least 30 minutes; alternatively, at least 1 hour; or alternatively, at least 2 hours. In yet other embodiments, the reaction time ranges from 5 minutes to 72 hours; alternatively, from 30 minutes to 48 hours; alternatively, from 1 hour minutes to 36 hours; or alternatively, from 2 hours and 24 hours.

DETD When a continuous reactor is used, a feed polyol weight unsaturated ester weight hourly space velocity ranging from 0.1 to 5 can be used to produce the desired ***thiol*** ester. Alternatively, the feed polyol weight hourly space velocity ranges between 0.1 to 5; alternatively, from 0.1 to 2. Alternatively, the feed polyol ester weight hourly space velocity is 0.1; alternatively, the feed polyol weight hourly space velocity is 0.25; or alternatively, the feed polyol weight hourly space velocity is 2.

DETD The reaction between the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative can be performed at any reaction pressure that maintains the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative in a liquid state.

In some embodiments, the reaction between the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative is performed at a pressure ranging from 0 psia to 2000 psia. In other embodiments, the reaction pressure ranges from 0 psia to 1000 psia; alternatively, from 0 psia and 500

psia; or alternatively, 0 psia to 300 psia.

DETD In some embodiments, the process to produce the ***thiol*** ester by reacting a polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative can further include a step to remove excess or residual polyol, ***thiol*** containing carboxylic acid, and/or ***thiol*** containing carboxylic acid derivative once the polyol has reacted with the ***thiol*** containing carboxylic acid or ***thiol*** containing carboxylic acid derivative. In some embodiments, the ***thiol*** ester is vacuum stripped. In some embodiments, the ***thiol*** ester is vacuum stripped at a temperature ranging between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the ***thiol*** ester is sparged with an inert gas to remove excess polyol, ***thiol*** containing carboxylic acid, and/or ***thiol*** containing carboxylic acid derivative. In some embodiments, the ***thiol*** ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged ***thiol*** ester comprises less than 5 excess polyol, ***thiol*** containing carboxylic acid, or ***thiol*** containing carboxylic acid derivative. In other embodiments, the stripped or sparged ***thiol*** ester comprises less than 2 weight percent excess polyol, ***thiol*** containing carboxylic acid, and/or ***thiol*** containing carboxylic acid derivative; alternatively, less than 1 weight percent excess polyol, ***thiol*** containing carboxylic acid, and/or ***thiol*** containing carboxylic acid derivative; or alternatively, less than 0.5 weight percent excess polyol, ***thiol*** containing carboxylic acid, and/or ***thiol*** containing carboxylic acid derivative.

DETD Process for Making Hydroxy ***Thiol*** Ester Composition
DETD The present invention advantageously provides processes for producing a hydroxy ***thiol*** ester as embodiments of the present invention.

As an embodiment, the present invention includes a process to produce the hydroxy ***thiol*** ester. The process comprises the

steps of

contacting hydrogen sulfide and an epoxidized unsaturated ester composition and reacting the hydrogen sulfide and the epoxidized unsaturated ester to form the hydroxy ***thiol*** ester. As another

embodiment of the present invention, another process to produce the

hydroxy ***thiol*** ester is provided. In this embodiment, the process comprises the steps of contacting a composition comprising a polyol with a composition comprising an hydroxy ***thiol*** containing carboxylic acid or an hydroxy ***thiol*** containing carboxylic acid derivative and reacting the polyol and the hydroxy ***thiol*** containing carboxylic acid or the hydroxy ***thiol*** containing carboxylic acid derivative to form the hydroxy ***thiol*** ester.

DETD Hydroxy ***Thiol*** Ester from Hydrogen Sulfide and an Epoxidized

Unsaturated Ester Composition

DETD As an embodiment of the present invention, the hydroxy ***thiol***

ester composition is produced by a process comprising the steps of

contacting hydrogen sulfide and an epoxidized unsaturated ester composition and reacting the hydrogen sulfide and the epoxidized unsaturated ester to produce the hydroxy ***thiol*** ester composition.

DETD In some embodiments, the epoxidized unsaturated ester composition

includes epoxidized unsaturated esters that have an average of at least

1 ester groups and an average of at least 1 ***epoxide*** groups per epoxidized unsaturated ester molecule.

DETD The process for producing or preparing the hydroxy ***thiol*** ester composition can be applied to any of the epoxidized unsaturated

esters described herein and used to produce any hydroxy ***thiol***

ester described herein. The process for producing the hydroxy ***thiol*** ester can also include any additional process steps or

process conditions as described herein. Additionally, the process for

producing the hydroxy ***thiol*** ester can form any hydroxy ***thiol*** ester described herein.

DETD In some aspects, the hydroxy ***thiol*** ester is produced by

contacting hydrogen sulfide with the epoxidized natural source oil under

the reaction conditions to form the hydroxy ***thiol*** ester in the

presence of an optional catalyst. In some embodiments, the catalyst can

be a heterogeneous catalyst or a homogeneous catalyst. Examples of

suitable catalysts are described herein. Additional types of suitable catalysts will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD The hydrogen sulfide to molar equivalents of ***epoxide*** groups in the epoxidized unsaturated ester (hereinafter "hydrogen sulfide to ***epoxide*** group molar ratio") utilized in the process to produce the hydroxy ***thiol*** ester can be any hydrogen sulfide to ***epoxide*** group molar ratio that produces the desired hydroxy ***thiol*** ester. The molar equivalents of epoxidized unsaturated ester epoxidized groups can be calculated by the equation:
##EQU2##

In this equation, EUES GMW is the average gram molecular weight of the epoxidized unsaturated ester, EUES Mass is the mass of the epoxidized unsaturated ester, and EUES ***Epoxide*** is the average number of ***epoxide*** groups per epoxidized unsaturated ester molecule. In some embodiments, the hydrogen sulfide to ***epoxide*** group molar ratio is greater than 0.2. In other embodiments, the hydrogen sulfide to ***epoxide*** group molar ratio is greater than 0.5; alternatively, greater than 1; or alternatively, greater than 2. In other embodiments, the hydrogen sulfide to ***epoxide*** group molar ratio ranges from 0.2 to 5; alternatively, from 0.5 to 4; or alternatively, from 0.75 to 3. In some embodiments, the hydrogen sulfide to ***epoxide*** group molar ratio is greater than 2. In other embodiments, the hydrogen sulfide to ***epoxide*** group molar ratio is greater than 5; alternatively, greater than 10; alternatively, greater than 15; or alternatively, greater than 20. In other embodiments, the hydrogen sulfide to ***epoxide*** group molar ratio can be from 0.2 to 500; alternatively, from 0.5 to 400; alternatively, from 1 to 300; alternatively, from 2 to 250; alternatively, 5 to 200; or alternatively, from 10 to 100.

DETD The time required for the reaction of the epoxidized unsaturated ester and hydrogen sulfide can be any time required to form the described hydroxy ***thiol*** ester. Generally, the time required for the reaction of the epoxidized unsaturated ester and hydrogen sulfide is at

least 15 minutes. In some embodiments, the time required for the reaction of the unsaturated ester and hydrogen sulfide ranges from 15 minutes to 72 hours; alternatively, from 30 minutes to 48 hours; alternatively, from 45 minutes to 36 hours.

DETD In some embodiments, the hydroxy ***thiol*** ester composition includes hydroxy ***thiol*** ester molecules that have an average of greater than 2.5 weight percent ***thiol*** sulfur. In some embodiments, the hydroxy ***thiol*** ester composition includes hydroxy ***thiol*** ester molecules that have an average of greater than 5 weight percent ***thiol*** sulfur. Alternatively, in some embodiments, the hydroxy ***thiol*** ester molecules have an average ranging from 8 to 10 weight percent ***thiol*** sulfur.

DETD In other aspects, the process producing the hydroxy ***thiol*** ester composition includes producing hydroxy ***thiol*** ester molecules having an average of greater than 40 percent of the sulfide-containing ester total side chains comprise a sulfide group.

Additional embodiments wherein the hydroxy ***thiol*** ester comprises a percentage of sulfide-containing ester total side chains are described herein.

DETD In embodiments, the process to produce the hydroxy ***thiol*** ester further comprises a step to remove residual hydrogen sulfide after reacting the hydrogen sulfide and the epoxidized unsaturated ester composition. In some embodiments, the hydroxy ***thiol*** ester is vacuum stripped. In some embodiments, the hydroxy ***thiol*** ester is vacuum stripped at a temperature ranging between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree.

C. In other embodiments, the hydroxy ***thiol*** ester is sparged with an inert gas to remove hydrogen sulfide. In some embodiments, the hydroxy ***thiol*** ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged hydroxy ***thiol*** ester comprises less than 0.1 weight percent hydrogen sulfide. In other embodiments, the stripped or sparged hydroxy ***thiol*** ester comprises less than 0.05 weight percent hydrogen sulfide; alternatively,

less than 0.025 weight percent hydrogen sulfide; or alternatively, less than 0.01 weight percent hydrogen sulfide.

DETD The reaction between the hydrogen sulfide and the epoxidized unsaturated ester can be performed at any temperature capable of forming the hydroxy ***thiol*** ester. In some embodiments, the epoxidized unsaturated ester and hydrogen sulfide can be reacted at a reaction temperature greater than -20.degree. C. In other embodiments, the reaction temperature is greater than 0.degree. C.; alternatively, greater than 20.degree. C.; alternatively, greater than 50.degree. C.; or alternatively, greater than 80.degree. C. In yet other embodiments, the reaction temperature ranges from -20.degree. C. to 200.degree. C.; alternatively, from 20.degree. C. to 170.degree. C.; or alternatively, from 80.degree. C. to 140.degree. C.

DETD In another aspect, the process to produce a hydroxy ***thiol*** ester produces a hydroxy ***thiol*** ester having an ***epoxide*** group to ***thiol*** group molar ratio less than 3.3. In another aspect, the process to produce a hydroxy ***thiol*** ester produces a hydroxy ***thiol*** ester having an ***epoxide*** group to ***thiol*** group molar ratio less than 2. Other hydroxy ***thiol*** ester ***epoxide*** group to ***thiol*** group molar ratios are described herein. Alternatively, the hydroxy ***thiol*** ester ***epoxide*** group to ***thiol*** group molar ratio can be less than 1.5; alternatively, less than 1.0; alternatively, less than 0.5; alternatively, less than 0.25; or alternatively, less than 0.1. In other embodiments, the hydroxy ***thiol*** ester can be substantially free of ***epoxide*** groups.

DETD In another aspect, the process to produce hydroxy ***thiol*** ester produces a hydroxy ***thiol*** ester wherein at least 20 percent of the side chains comprise an .alpha.-hydroxy ***thiol*** group. Other hydroxy ***thiol*** ester embodiments wherein the hydroxy ***thiol*** ester contains a percentage of side chains comprising .alpha.-hydroxy ***thiol*** groups are described herein.

DETD Hydroxy ***Thiol*** Ester from a Polyol and a Hydroxy ***Thiol*** Containing Carboxylic Acid Derivative

DETD As another embodiment of the present invention, another process

to prepare the hydroxy ***thiol*** ester is advantageously provided. In this embodiment, the process includes the steps of contacting a composition comprising a polyol with a composition comprising a hydroxy ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative and reacting the polyol and hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid to form a hydroxy ***thiol*** ester composition. This process can be applied to any polyol, any hydroxy ***thiol*** containing carboxylic acid, or any ***thiol*** containing carboxylic acid derivative described herein. The process for producing the hydroxy ***thiol*** ester composition can also include any additional process steps or process conditions described herein. Additionally, the process for producing the hydroxy ***thiol*** ester composition can form any ***thiol*** ester described herein.

DETD In some embodiments, the hydroxy ***thiol*** ester composition includes hydroxy ***thiol*** ester molecules that have an average of at least 1 ester groups per hydroxy ***thiol*** ester molecule and an average of at least 1 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule.

DETD The polyol used to produce the hydroxy ***thiol*** ester by contacting a polyol and a hydroxy ***thiol*** carboxylic acid and/or hydroxy ***thiol*** carboxylic acid equivalent (for example a hydroxy ***thiol*** carboxylic acid methyl ester) can be any polyol or mixture of polyols that can produce the described ***thiol*** containing ester.

DETD In one aspect, the polyol used to produce the hydroxy ***thiol*** ester can comprise from 2 to 20 carbon atoms. In other embodiments, the polyol comprises from 2 to 10 carbon atoms; alternatively from 2 to 7 carbon atoms; alternatively from 2 to 5 carbon atoms. In further embodiments, the polyol may be a mixture of polyols having an average of 2 to 20 carbon atoms; alternatively, an average of from 2 to 10 carbon atoms; alternatively, an average of 2 to 7 carbon atoms; alternatively an average of 2 to 5 carbon atoms.

DETD In another aspect, the polyol used to produce the hydroxy ***thiol*** ester can have any number of hydroxy groups needed to produce the hydroxy ***thiol*** ester as described herein. In some embodiments,

the polyol has 2 hydroxy groups; alternatively, 3 hydroxy groups; alternatively, 4 hydroxy groups; alternatively, 5 hydroxy groups; or alternatively, 6 hydroxy groups. In other embodiments, the polyol comprises at least 2 hydroxy groups; alternatively at least 3 hydroxy groups; alternatively, at least 4 hydroxy groups; alternatively, at least 5 hydroxy groups; at least 6 hydroxy groups. In yet other embodiments, the polyol comprises from 2 to 8 hydroxy groups; alternatively, from 2 to 4 hydroxy groups; or alternatively from 4 to 8 hydroxy groups.

DETD In further aspects, the polyol used to produce the hydroxy ***thiol*** ester is a mixture of polyols. In an embodiment, the mixture of polyols has an average of at least 1.5 hydroxy groups per polyol molecule. In other embodiments, the mixture of polyols has an average of at least 2 hydroxy groups per polyol molecule; alternatively, an average of at least 2.5 hydroxy groups per polyol molecule; alternatively, an average of at least 3.0 hydroxy groups per polyol molecule; or alternatively, an average of at least 4 hydroxy groups per polyol molecule. In yet another embodiment, the mixture of polyols has an average of 1.5 to 8 hydroxy groups per polyol molecule; alternatively, an average of 2 to 6 hydroxy groups per polyol molecule; alternatively, an average of 2.5 to 5 hydroxy groups per polyol molecule; alternatively, an average of 3 to 4 hydroxy groups per polyol molecule; alternatively, an average of 2.5 to 3.5 hydroxy groups per polyol molecule; or alternatively, an average of 2.5 to 4.5 hydroxy groups per polyol molecule.

DETD In yet another aspect, the polyol or mixture of polyols used to produce the hydroxy ***thiol*** ester has a molecular weight or average molecular weight less than 500. In other embodiments, the polyol or mixture of polyols have a molecular weight or average molecular weight less than 300; alternatively less than 200; alternatively, less than 150; or alternatively, less than 100.

DETD The hydroxy ***thiol*** carboxylic acid and/or hydroxy ***thiol*** carboxylic acid equivalent used to produce the hydroxy ***thiol*** ester by contacting a polyol and a hydroxy ***thiol*** carboxylic acid and/or hydroxy ***thiol*** carboxylic acid equivalent can be any hydroxy ***thiol*** carboxylic acid mixture comprising hydroxy ***thiol*** carboxylic acids, hydroxy

hydroxy ***thiol*** carboxylic acid equivalent or mixture comprising
described ***thiol*** carboxylic acid equivalents that can produce the
hydroxy ***thiol*** containing ester. When talking about the
characteristics hydroxy ***thiol*** carboxylic acid
equivalent or
hydroxy ***thiol*** carboxylic acid equivalents, properties
such as
number of carbon atoms, average number of carbon atom, molecular
weight
or average molecular weight, number of ***thiol*** group, and
average number of ***thiol*** groups, one will understand the
these
properties will apply to the portion of the ***thiol***
carboxylic
acid equivalent which adds to the polyol to form the
thiol
ester.

DETD In an aspect, the hydroxy ***thiol*** carboxylic acid and/or
hydroxy ***thiol*** carboxylic acid equivalent used to
produce the
thiol ester comprises from 2 to 28 carbon atoms. In an
embodiment, the hydroxy ***thiol*** carboxylic acid and/or
hydroxy ***thiol*** carboxylic acid equivalents comprises from 4 to
26 carbon
atoms; alternatively, from 8 to 24 carbon atoms; alternatively,
from 12
to 24 carbon atoms; or alternatively, from 14 to 20 carbon atoms.
In
other embodiments, a mixture comprising hydroxy ***thiol***
carboxylic acids and/or mixture comprising hydroxy ***thiol***
carboxylic acid equivalents has an average of 2 to 28 carbon
atoms per
carboxylic acid and/or carboxylic acid equivalent; alternatively,
from 4
to 26 carbon per carboxylic acid and/or carboxylic acid
equivalent;
alternatively, from 8 to 24 carbon atoms per carboxylic acid
and/or
carboxylic acid equivalent; alternatively, from 12 to 24 carbon
atoms
per carboxylic acid and/or carboxylic acid equivalent; or
alternatively,
from 14 to 20 carbon atoms per carboxylic acid and/or carboxylic
acid
equivalent.

DETD In another aspect, the hydroxy ***thiol*** carboxylic acid
and/or
hydroxy ***thiol*** carboxylic acid equivalent used to
produce the
thiol ester has at least 1 ***thiol*** group;
alternatively
2 ***thiol*** groups. In some embodiments, a mixture
comprising
hydroxy ***thiol*** carboxylic acids and/or mixture
comprising
hydroxy ***thiol*** carboxylic acid equivalents has an
average of

from 0.5 to 3 ***thiol*** groups per carboxylic acid and/or carboxylic acid equivalent; alternatively, an average of from 1 to 2 ***thiol*** groups per carboxylic acid and/or carboxylic acid equivalent.

DETD In another aspect, the hydroxy ***thiol*** carboxylic acid and/or hydroxy ***thiol*** carboxylic acid equivalent used to produce the ***thiol*** ester has at least 1 hydroxy group; alternatively, at least 2 hydroxy groups. In some embodiments, a mixture comprising hydroxy ***thiol*** carboxylic acids and/or mixture comprising hydroxy ***thiol*** carboxylic acid equivalents has an average of from 0.5 to 3 hydroxy groups per carboxylic acid and/or carboxylic acid equivalent; alternatively, an average of from 1 to 2 hydroxy groups per carboxylic acid and/or carboxylic acid equivalent.

DETD In another aspect, the hydroxy ***thiol*** carboxylic acid and/or hydroxy ***thiol*** carboxylic acid equivalent used to produce the hydroxy ***thiol*** ester has a molecular weight greater than 100; alternatively greater than 180; alternatively greater than 240; or alternatively greater than 260. In other embodiments, the hydroxy ***thiol*** carboxylic acid and/or hydroxy ***thiol*** carboxylic acid equivalent has a molecular weight from 100 to 500; alternatively, from 120 to 420; alternatively, from 180 to 420; alternatively, from 240 to 420; a mixture or alternatively, from 260 to 360. In some embodiments, a mixture comprising hydroxy ***thiol*** carboxylic acids and/or mixture comprising hydroxy ***thiol*** carboxylic acid equivalents has an average molecular weight greater than 100 per carboxylic acid and/or carboxylic acid equivalent; alternatively greater than 180 per carboxylic acid and/or carboxylic acid equivalent; alternatively greater than 240 per carboxylic acid and/or carboxylic acid equivalent; or alternatively greater than 260 per carboxylic acid and/or carboxylic acid equivalent. In yet other embodiments, the mixture comprising hydroxy ***thiol*** carboxylic acid and/or mixture comprising hydroxy ***thiol*** carboxylic acid equivalents has an average molecular weight from 100 to 500 per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 120 to 420 per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 180 to 420 per carboxylic acid and/or carboxylic acid equivalent;

alternatively, from 240 to 420 per carboxylic acid and/or carboxylic acid equivalent; a mixture or alternatively, from 260 to 360 per carboxylic acid and/or carboxylic acid equivalent.

DETD In some aspects, the reaction between the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative occurs in the presence of a solvent. In other aspects, the reaction between the polyol and the hydroxy ***thiol*** containing carboxylic acid derivative occurs in the substantial absence of a solvent. In aspects wherein the reaction between the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative occurs in the presence of a solvent, the solvent is selected from the group consisting of an aliphatic hydrocarbon, an ether, an aromatic compound, or any combination thereof. Generally, the solvent, regardless of its chemical class, includes from 1 to 20 carbon atoms; alternatively, from 3 to 10 carbon atoms. When the solvent includes the aliphatic hydrocarbon, the aliphatic hydrocarbon is butane, isobutane, pentane, hexane, heptane, octane, or any mixture thereof. When the solvent includes the aromatic compound, the aromatic compound is benzene, toluene, xylene, ethylbenzene, or any mixture thereof.

When the solvent includes the ether, the ether is diethyl ether, dipropyl ether, tetrahydrofuran, and any mixture thereof.

DETD When a solvent is used for the reaction between the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative, the quantity of solvent can be any amount that facilitates the reaction. In some embodiments, the mass of the solvent is less than 30 times the mass of the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative. In other embodiments, the mass of the solvent is less than 20 times the mass of the hydroxy ***thiol*** ester; alternatively, less than 15 times the mass of the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative; alternatively, less than 10 times the mass of the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative; or alternatively, less than 5 times

the mass of the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative. In other embodiments, the mass of the solvent is from 2 times to 20 times the mass of the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative; alternatively, from 3 times to 15 times the mass of the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative; or alternatively, from 5 times to 10 times the mass of the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative.

DETD The equivalents of hydroxy ***thiol*** containing carboxylic acid derivative and/or hydroxy ***thiol*** containing carboxylic acid derivative carboxylic acid groups to equivalents of polyol hydroxy groups molar ratio (hereinafter referred to as "carboxylic acid group to polyol hydroxy group molar ratio") utilized in the process to produce the hydroxy ***thiol*** ester can be any carboxylic acid group to polyol hydroxy group molar ratio that produces the desired hydroxy ***thiol*** ester. In some embodiments, the carboxylic acid group to polyol hydroxy group molar ratio is greater than 0.4. In other embodiments, the carboxylic acid group to polyol hydroxy group molar ratio is greater than 0.6; alternatively, greater than 0.8; alternatively, greater than 1; or alternatively, greater than 1.1. In other embodiments, the carboxylic acid group to polyol hydroxy group molar ratio ranges from 0.4 to 1.3; alternatively, from 0.6 to 1.2, or alternatively, from 0.8 to 1.1.

DETD In some aspects, the reaction between the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative is catalyzed. In some embodiments, the catalyst is a mineral acid, such as sulfuric or phosphoric acid. In other embodiments, the catalyst is an organic acid. In embodiments, for example, the organic acid is methane sulfonic acid or toluene sulfonic acid. Other suitable types of catalyst will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD The reaction of the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative can occur in a batch reactor or a continuous reactor, as described herein. The reaction between the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative can be performed at any temperature capable of forming the hydroxy ***thiol*** ester.

In some embodiments, the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative can be reacted at a temperature greater than 20.degree.

C. In other embodiments, the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative can be reacted at a temperature greater than 50.degree. C.; alternatively, greater than 75.degree. C.; or alternatively, greater than 100.degree. C. In yet other embodiments, the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative can be reacted at a temperature from 20.degree. C. to 250.degree. C.; alternatively, from 50.degree. C. to 200.degree. C.; alternatively, from 75.degree. C. to 175.degree. C.; or alternatively, from 100.degree. C. to 150.degree..

DETD The time required for the reaction of the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative can be any time required to form the described hydroxy ***thiol*** ester composition.

Generally, the reaction time is at least 5 minutes. In some embodiments, the reaction time is at least 30 minutes; alternatively, at least 1 hour; or alternatively, at least 2 hours. In yet other embodiments, the reaction time ranges from 5 minutes to 72 hours; alternatively, from 30 minutes

to 48 hours; alternatively, from 1 hour minutes to 36 hours; or alternatively, from 2 hours and 24 hours.

DETD The reaction between the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative can be performed at any reaction pressure that maintains the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing

carboxylic acid derivative in a liquid state. In some embodiments, the reaction pressure ranges from 0 psia to 2000 psia. In other embodiments, the reaction pressure ranges from 0 psia to 1000 psia; alternatively, from 0 psia and 500 psia; or alternatively, from 0 psia to 300 psia. DETD In some embodiments, the process to produce the hydroxy ***thiol*** ester composition by reacting a polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative can further include a step to remove excess or residual polyol, hydroxy ***thiol*** containing carboxylic acid, and/or hydroxy ***thiol*** containing carboxylic acid derivative once the polyol has reacted with the hydroxy ***thiol*** containing carboxylic acid or hydroxy ***thiol*** containing carboxylic acid derivative. In some embodiments, the ***thiol*** ester is vacuum stripped. In some embodiments, the hydroxy ***thiol*** ester is vacuum stripped at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the hydroxy ***thiol*** ester is sparged with an inert gas to remove excess polyol, hydroxy ***thiol*** containing carboxylic acid, and/or hydroxy ***thiol*** containing carboxylic acid derivative. In some embodiments, the hydroxy ***thiol*** ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C., or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged hydroxy ***thiol*** ester oil comprises less than 5 excess polyol, hydroxy ***thiol*** containing carboxylic acid, or hydroxy ***thiol*** containing carboxylic acid derivative. In other embodiments, the stripped or sparged hydroxy ***thiol*** ester oil comprises less than 2 weight percent excess polyol, hydroxy ***thiol*** containing carboxylic acid, and/or hydroxy ***thiol*** containing carboxylic acid derivative; less than 1 weight percent excess polyol, hydroxy ***thiol*** containing carboxylic acid, and/or

hydroxy ***thiol*** containing carboxylic acid derivative; or alternatively, less than 0.5 weight percent excess polyol, hydroxy ***thiol*** containing carboxylic acid, and/or hydroxy ***thiol*** containing carboxylic acid derivative.

DETD A method of making a thioacrylate containing ester composition is advantageously provided as another embodiment of the present invention.

The process for producing the thioacrylate containing ester comprising contacting a ***thiol*** ester with an acrylate and converting at least one ***thiol*** group to a ***thiol*** acrylate group. The process can be applied to any of the ***thiol*** esters described herein and used to any thioacrylate ester described herein. The process for producing the thioacrylate ester can also include any additional process steps or process conditions described herein.

DETD The acrylate compound can be any acrylate compound capable of reacting with a ***thiol*** group to form the ***thiol*** acrylate group.

In some embodiments, the acrylate compound can be an acrylic halide. In other embodiments, the acrylate compound can be an acrylic acid. In yet other embodiments, the acrylate compound can be an acrylic anhydride.

DETD In some aspects, the conversion of the ***thiol*** group to a thioacrylate group occurs in the presence of a solvent. In other aspects the conversion of the ***thiol*** group to a thioacrylate group occurs in the substantial absence of a solvent. In aspects wherein the conversion of the ***thiol*** group to a thioacrylate group occurs

in the presence of a solvent, the solvent may be an aliphatic hydrocarbon, an ether, and aromatic compound. Generally, the solvent, regardless of its chemical class, includes from 1 to 20 carbon atoms; or alternatively, from 3 to 10 carbon atoms. When the solvent includes the aliphatic hydrocarbon, the aliphatic hydrocarbon is butane, isobutane, pentane, hexane, heptane, octane, or any mixture thereof. When the

solvent includes the aromatic compound, the aromatic compound is benzene, toluene, xylene, ethylbenzene, or any mixture thereof. When the solvent includes the ether, the ether is diethyl ether, dipropyl ether, tetrahydrofuran, or any mixture thereof.

DETD When a solvent is used for the conversion of the ***thiol*** group to a thioacrylate group, the quantity of solvent can be any amount that facilitates the reaction. In some embodiments, the mass of the solvent is less than 30 times the mass of the ***thiol*** ester. In other embodiments, the mass of the solvent is less than 20 times the mass of the ***thiol*** ester; alternatively, less than 15 times the mass of the ***thiol*** ester; alternatively, less than 10 times the mass of the ***thiol*** ester; or alternatively, less than 5 times the mass of the ***thiol*** ester. In other embodiments, the mass of the solvent is from 2 times to 20 times the mass of the ***thiol*** ester; alternatively, from 3 times to 15 times the mass of the ***thiol*** ester; alternatively, 4 times to 15 times the mass of the ***thiol*** ester; or alternatively, from 5 times to 10 times the mass of the ***thiol*** ester.

DETD In some aspects the conversion of the ***thiol*** group to the thioacrylate group occurs in the presence of a catalyst. In some embodiments, the catalyst is homogeneous. In some embodiments, the catalyst is an organic amine. Examples of suitable organic amines include triethylamine, tripropylamine, tributylamine, and pyridine. In other embodiments, the catalyst is heterogeneous. Examples of suitable catalysts include Amberlyst A-21 and Amberlyst A-26. Other suitable catalysts will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD The conversion of the ***thiol*** group to a thioacrylate group can be performed at any conversion temperature that is capable of converting the ***thiol*** group to a thioacrylate group. In some embodiments, the conversion temperature is greater than -20.degree. C. In other embodiments, the conversion temperature is greater than 0.degree. C.; alternatively, greater than 20.degree. C.; alternatively, greater than 50.degree. C.; alternatively, greater than 80.degree. C.; or alternatively, greater than 100.degree. C. In yet other embodiments, the conversion temperature ranges from -20.degree. C. to 250.degree. C.; alternatively, from 20.degree. C. to 200.degree. C.; or alternatively, from 50.degree. C. to 150.degree. C.

DETD The conversion time required for the conversion of the ***thiol*** group to a thioacrylate group can be any time required to form the described thioacrylate containing ester. Generally, the conversion time is at least 5 minutes. In some embodiments, the conversion time is at least 15 minutes; alternatively, at least 30 minutes; alternatively, at least 45 minutes; or alternatively, at least 1 hour. In other embodiments, the conversion time ranges from 15 minutes to 12 hours; alternatively, from 30 minutes to 6 hours; or alternatively, from 45 minutes to 3 hours.

DETD The conversion of the ***thiol*** group to a thioacrylate group can be performed at any conversion pressure that maintains the ***thiol*** ester and the acrylate compound in the liquid state. In some embodiments, the conversion pressure ranges from 0 psia to 2000 psia. In other embodiments, the conversion pressure ranges from 0 psia to 1000 psia; or alternatively, from 0 psia to 500 psia.

DETD Process for Producing Cross-Linked ***Thiol*** Ester
DETD As an embodiment of the present invention, a process for producing a cross-linked ***thiol*** ester composition is advantageously provided. Minimally, in some embodiments, the process to produce the cross-linked ***thiol*** ester composition comprises contacting a ***thiol*** ester composition with an oxidizing agent and reacting the ***thiol*** ester composition and an oxidizing agent to form the ***thiol*** ester oligomer having at least two ***thiol*** ester monomers connected by a polysulfide linkage having the structure --S_{sub}Q--, wherein Q is an integer greater than 1. The disclosed method may be applied to any ***thiol*** ester described herein to produce any cross-linked ***thiol*** ester composition as described herein. The process to produce the cross-linked ***thiol*** ester composition can also include any additional process steps or process conditions as described herein.

DETD When elemental sulfur is used as the oxidizing agent, the quantity of elemental sulfur utilized to form the cross-linked ***thiol*** ester composition is determined as a function of the ***thiol*** sulfur content of the ***thiol*** ester composition. In an aspect, the

weight ratio of elemental sulfur to ***thiol*** sulfur in the ***thiol*** ester composition is at least 0.5. In some embodiments, the weight ratio of elemental sulfur to ***thiol*** sulfur in the ***thiol*** ester composition is at least 5; alternatively, at least 10, alternatively, at least 15, or alternatively, at least 20. In other embodiments, the weight ratio of elemental sulfur to ***thiol*** sulfur in the ***thiol*** ester composition ranges from 0.5 to 32; alternatively, ranges from 1 to 24; alternatively, ranges from 2 to 16; or alternatively, ranges from 3 to 10.

DETD In an aspect, the reaction of the ***thiol*** ester and elemental sulfur occurs in the presence of a catalyst. The catalyst can be any catalyst that catalyzes the formation of the polysulfide linkage between at least two ***thiol*** ester monomers. In some embodiments, the catalyst is an amine. In further embodiments, the catalyst is a tertiary amine.

DETD The formation of the cross-linked ***thiol*** ester can occur in a batch reactor or a continuous reactor, as described herein. The formation of the cross-linked ***thiol*** ester can occur at any temperature capable of forming the ***thiol*** ester. In some embodiments, the formation of the cross-linked ***thiol*** ester can occur at a temperature greater than 25.degree. C. In other embodiments, the formation of the cross-linked ***thiol*** ester can occur at a temperature greater than 50.degree. C.; alternatively, greater than 70.degree. C.; or alternatively, greater than 80.degree. C. In yet other embodiments, the formation of the cross-linked ***thiol*** ester occurs at a temperature from 25.degree. C. to 150.degree. C.; alternatively, from 50.degree. C. to 150.degree. C.; alternatively, from 70.degree. C. to 120.degree. C.; or alternatively, from 80.degree. C. to 110.degree. C.

DETD The time required to form the cross-linked ***thiol*** ester can be any time required to form the desired cross-linked ***thiol*** ester. Generally, the time required to form the cross-linked ***thiol*** ester is at least 15 minutes. In some embodiments, the time required to form the cross-linked ***thiol*** ester is at least 30 minutes; alternatively, at least 1 hour; or alternatively, at

least 2

hours. In yet other embodiments, the time required to form the cross-linked ***thiol*** ester ranges from 15 minutes to 72 hours; alternatively, from 30 minutes to 48 hours; alternatively, from 1 hour minutes to 36 hours; or alternatively, from 2 hours and 24 hours.

DETD In embodiments, the process to produce the cross-linked ***thiol*** ester further comprises a step to remove residual hydrogen sulfide. In

some embodiments the cross-linked ***thiol*** ester is vacuum stripped. In some embodiments, the cross-linked ***thiol*** ester is vacuum stripped at a temperature between 25.degree. C. and 250.degree.

C.; alternatively, between 50.degree. C. and 200.degree. C.; or alternatively, 75 and 150.degree. C. In some embodiments, the cross-linked ***thiol*** ester oil is sparged with an inert gas to

remove residual hydrogen sulfide. In other embodiments, the cross-linked ***thiol*** ester is sparged with an inert gas at a temperature

between 25.degree. C. and 250.degree. C.; alternatively, between 50.degree. C. and 200.degree. C.; or alternatively, between 75 and

150.degree. C. In yet other embodiments, the vacuum stripping is performed while sparging the cross-linked ***thiol*** ester with an

inert gas. In yet other embodiments, the vacuum stripping is performed while sparging the cross-linked ***thiol*** ester an inert gas at a

temperature between 25.degree. C. and 250.degree. C.; alternatively, between 50.degree. C. and 200.degree. C.; or alternatively, 75 and

150.degree. C. In some embodiments, the inert gas is nitrogen. DEDT Generally, the stripped or sparged cross-linked ***thiol*** ester

comprises less than 0.1 weight percent hydrogen sulfide. In other embodiments, the stripped or sparged ***thiol*** -containing ester

oil comprises less than 0.05 weight percent hydrogen sulfide; alternatively, less than 0.025 weight percent hydrogen sulfide; or

alternatively, less than 0.01 weight percent hydrogen sulfide. DEDT The present invention advantageously provides processes for producing

sulfide-containing esters as embodiments of the present invention.

Generally, the sulfide-containing esters can be prepared by two processes. As an embodiment of the present invention, the first process

used to produce a sulfide-containing ester comprises contacting an

unsaturated ester and a ***mercaptan*** and reacting the unsaturated ester and ***mercaptan*** to form a sulfide-containing ester.

As

another embodiment of the present invention, the second process used to produce a sulfide-containing ester comprises contacting an epoxidized unsaturated ester and a ***mercaptan*** sulfide and reacting the unsaturated ester and ***mercaptan*** to form a sulfide-containing ester. Additional aspects of the two sulfide-containing ester production processes are described below.

DETD The sulfide-containing esters and sulfide-containing ester compositions

described herein can be produced by a process comprising contacting a

mercaptan and an unsaturated ester and reacting the ***mercaptan*** and the unsaturated ester to form a sulfide-containing ester. The process can be applied to any of the unsaturated esters and

mercaptans described herein. The process for producing the sulfide-containing ester can also include any additional process steps or process conditions described herein. Additionally, the process for producing the sulfide-containing ester can form any sulfide-containing ester described herein.

DETD In some aspects, the reaction between the ***mercaptan*** and the unsaturated ester occurs in the presence of a solvent. In other aspects

the reaction between the ***mercaptan*** and the unsaturated ester occurs in the substantial absence of a solvent. When the reaction occurs in the presence of a solvent, the solvent is selected from an aliphatic hydrocarbon, an ether, an aromatic compound, an alcohol, or any combination thereof. Generally, the solvent, regardless of its chemical class, can comprise from 1 to 20 carbon atoms; alternatively, from 3 to 10 carbon atoms. When the solvent includes an aliphatic hydrocarbon, the aliphatic hydrocarbon is butane, isobutane, pentane, hexane, heptane, octane, or any mixture thereof. When the solvent includes an aromatic compound, the aromatic compound is benzene, toluene, xylene, ethylbenzene, or any mixture thereof. When the solvent includes an

alcohol, the alcohol is methanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-2-proanol, or any mixture thereof. When the solvent

includes an ether, the ether is diethyl ether, dipropyl ether, tetrahydrofuran, or any mixture thereof.

DETD When a solvent is used for the reaction between the ***mercaptan*** and the unsaturated ester, the quantity of solvent can be any amount that facilitates the reaction, as understood by those of skill in the art. In some embodiments, the mass of the solvent is less than 30 times the mass of the unsaturated ester. In other embodiments, the mass of the solvent is less than 20 times the mass of the unsaturated ester; alternatively, less than 15 times the mass of the unsaturated ester; alternatively, less than 10 times the mass of the unsaturated ester; or alternatively, less than 5 times the mass of the unsaturated ester. In other embodiments, the mass of the solvent is from 2 times to 20 times the mass of the unsaturated ester; alternatively, from 3 times to 15 times the mass of the unsaturated ester; alternatively, from 4 times to 15 times the mass of the unsaturated ester; or alternatively, from 5 times to 10 times the mass of the unsaturated ester.

DETD The molar ratio of ***mercaptan*** to molar equivalents of unsaturated ester carbon-carbon double bonds (herein after " ***mercaptan*** to carbon-carbon double bond molar ratio") utilized in the process to produce the sulfide-containing ester can be any ***mercaptan*** to carbon-carbon double bond molar ratio that produces the desired sulfide-containing ester. The molar equivalents of unsaturated ester carbon-carbon double bonds is calculated by the equation: ##EQU3## In this equation, UES GMW is the average gram molecular weight of the unsaturated ester, UES Mass is the mass of the unsaturated ester, and UES C.dbd.C is the average number of double bonds per unsaturated ester molecule. In some embodiments, the ***mercaptan*** to carbon-carbon double bond molar ratio is greater than 0.25. In other embodiments, the ***mercaptan*** to carbon-carbon double bond molar ratio is greater than 0.5; alternatively, greater than 0.75; alternatively, greater than 1; alternatively, greater than 1.25; or alternatively, greater than 1.5. In other embodiments, the ***mercaptan*** to carbon-carbon double bond molar ratio can range from 0.25 to 2; alternatively, from 0.5 to 1.5, or alternatively, from 0.75 to 1.25.

DETD In some aspects the reaction between the ***mercaptan*** and the ***mercaptan*** unsaturated ester is catalyzed. The reaction of the ***mercaptan*** and the unsaturated ester can be catalyzed by a heterogeneous catalyst

the or homogeneous catalyst, as described herein. In some aspects, the reaction between the ***mercaptan*** and the unsaturated ester is initiated by a free radical initiator or ultraviolet radiation, as described herein.

DETD The free radical initiator can be any free radical initiator capable of forming free radicals under thermal or light photolysis. Generally, the free radical initiator is selected from the general class of compounds having a --N.dbd.N-- group or a --O--O-- group. Specific classes of free radical initiators include diazo compounds, dialkyl peroxides, hydroperoxides, and peroxy esters. Specific initiators include azobenzene, 2,2'-azobis(2-methylpropionitrile, 4,4'-azobis(4-cyanovaleic acid), 1,1'-azobis(cyclohexanecarbonitrile), 2,2'-azobis(2methylpropane), 2,2'-azobis(2-methylpropionamidine) dihydro-chloride, methylpropionitrile, azodicarboxamide, tert-butyl hydroperoxide, di-tert-butyl peroxide, octylperbenzoate. In some embodiments, the free radical initiated reaction of the ***mercaptan*** and the unsaturated ester is performed at a reaction temperature within .+- .50.degree. C. of the 1 hour half life of the free radical initiator. In other embodiments, the reaction temperature is within .+- .25.degree. C. of the 1 hour half life of the free radical initiator; alternatively, the reaction temperature is within .+- .20.degree. C. of the 1 hour half life of the free radical initiator; alternatively, the reaction temperature is within .+- .15.degree. C. of the 1 hour half life of the free radical initiator; or alternatively, the reaction temperature is within .+- .10.degree. C. of the 1 hour half life of the free radical initiator. In embodiments where the free radical initiated reaction of the ***mercaptan*** and the unsaturated ester is initiated by light photolysis, the light can be any light capable creating free radicals. In some embodiments, the light is UV radiation. Other sources of light capable of creating free radicals will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD In another aspect, the reaction of the ***mercaptan*** and the unsaturated ester is initiated by UV radiation. In these embodiments, the UV radiation may be any UV radiation capable of initiating the reaction of the ***mercaptan*** and the unsaturated ester. In

some embodiments, the UV radiation is generated by a medium pressure mercury lamp.

DETD The reaction of the ***mercaptan*** and the unsaturated ester can occur in a batch reactor or a continuous reactor. Any of the batch or continuous reactors described herein can be used in this reaction. Other suitable reactors will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD The reaction time for reacting the ***mercaptan*** and the unsaturated ester can be any time required to form the sulfide-containing ester. Generally, the reaction time is at least 5 minutes. In some embodiments, the reaction time ranges from 5 minutes to 72 hours; alternatively, from 10 minutes to 48 hours; or alternatively, from 15 minutes to 36 hours.

DETD In some embodiments, the process to produce the sulfide-containing ester further comprises a step to remove any residual ***mercaptan*** that remains after reacting the ***mercaptan*** and the unsaturated ester. In some embodiments, the sulfide-containing ester is vacuum stripped to remove the residual ***mercaptan***. In some embodiments, the sulfide-containing ester is vacuum stripped at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the sulfide-containing ester is sparged with an inert gas to remove the residual ***mercaptan***. In some embodiments, the sulfide-containing ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged sulfide-containing ester comprises less than 5 weight percent of the ***mercaptan***. In other embodiments, the stripped or sparged sulfide-containing ester comprises less than 2 weight percent of the ***mercaptan***; alternatively, less than 1 weight percent of the ***mercaptan***; or alternatively, less than 0.5 weight percent of the ***mercaptan***.

DETD The reaction between the ***mercaptan*** and the unsaturated ester can be performed at any temperature capable of forming the sulfide-containing ester. In some embodiments, the

mercaptan

and the unsaturated ester can be reacted at a reaction temperature of greater than -20.degree. C. In other embodiments, the reaction temperature is greater than 0.degree. C.; alternatively, greater than

20.degree. C.; alternatively, greater than 50.degree. C.; alternatively,

greater than 80.degree. C.; or alternatively, greater than 100.degree.

C. In yet other embodiments, the ***mercaptan*** and the unsaturated ester can be reacted at a temperature from -20.degree. C. to 250.degree.

C.; alternatively, from 20.degree. C. to 200.degree. C.; or alternatively, from 80.degree. C. to 160.degree. C.

DETD The reaction between the ***mercaptan*** and the unsaturated ester can be performed at any pressure that maintains the ***mercaptan***

and the unsaturated ester in a substantially liquid state. In some

embodiments, the ***mercaptan*** and the unsaturated ester can be performed at a reaction pressure ranging from 0 psig to 2000

psig. In other embodiments, the reaction pressure ranges from 0 psig to 1000

psig; alternatively, from 0 psig to 500 psig; or alternatively, from 0

psig to 200 psig.

DETD Using the disclosed process, sulfide-containing ester having a low carbon-carbon double bond to sulfide group molar ratio can be produced.

In an aspect, the process for producing the sulfide-containing ester forms a sulfide-containing ester having a carbon-carbon double bond to

thiol group molar ratio of less than 1.5. Additional carbon-carbon double bond to sulfide group molar ratios are disclosed

herein.

DETD As another embodiment of the present invention, another process for

producing a class of sulfide-containing esters, which includes hydroxy

sulfide-containing esters, is advantageously provided. In this embodiment, the hydroxy sulfide-containing esters and hydroxy sulfide-containing ester compositions can be produced by a process

comprising the steps of contacting a ***mercaptan*** and an epoxidized unsaturated ester and reacting the ***mercaptan***

and

the epoxidized unsaturated ester to produce or form the hydroxy sulfide-containing ester. The process can be applied to any ***mercaptan*** and/or any epoxidized unsaturated esters described

herein. The process for producing the hydroxy sulfide-containing ester

can also include any additional process steps or process conditions as described herein. Additionally, the process for producing the hydroxy sulfide-containing ester can form any hydroxy sulfide-containing ester as described herein.

DETD In some aspects, the reaction between the ***mercaptan*** and the unsaturated ester occurs in the presence of a solvent. In other aspects the reaction between the ***mercaptan*** and the unsaturated ester occurs in the substantial absence of a solvent. When the reaction occurs in the presence of a solvent, the solvent is selected from an aliphatic hydrocarbon, an ether, an aromatic compound, or any combination thereof.

Generally, the solvent, regardless of its chemical class, can comprise from 1 to 20 carbon atoms; alternatively, from 3 to 10 carbon atoms.

When the solvent includes an aliphatic hydrocarbon, the aliphatic hydrocarbon is butane, isobutane, pentane, hexane, heptane, octane, or any mixture thereof. When the solvent includes an aromatic compound, the aromatic compound is benzene, toluene, xylene, ethylbenzene, or any mixture thereof. When the solvent includes an ether, the ether is diethyl ether, dipropyl ether, tetrahydrofuran, or any mixture thereof.

DETD When a solvent is used for the reaction between the ***mercaptan*** and the epoxidized unsaturated ester, the quantity of solvent can be any amount that facilitates the reaction, as understood by those of skill in the art. In some embodiments, the mass of the solvent is less than 30 times the mass of the epoxidized unsaturated ester. In other embodiments, the mass of the solvent is less than 20 times the mass of the epoxidized unsaturated ester; alternatively, less than 15 times the mass of the epoxidized unsaturated ester; alternatively, less than 10 times the mass of the epoxidized unsaturated ester; or alternatively, less than 5 times the mass of the epoxidized unsaturated ester.

In other embodiments, the mass of the solvent is from 2 times to 20 times the mass of the epoxidized unsaturated ester; alternatively, from 3 times to 15 times the mass of the epoxidized unsaturated ester; alternatively, from 4 times to 15 times the mass of the epoxidized unsaturated ester;

or alternatively, from 5 times to 10 times the mass of the epoxidized unsaturated ester.

DETD The reaction of the ***mercaptan*** and the epoxidized unsaturated ester can occur using any ***mercaptan*** to molar equivalents of ***epoxide*** groups in the epoxidized unsaturated ester (hereinafter referred to as " ***mercaptan*** to ***epoxide*** group molar ratio") that is capable of producing the herein described .alpha.-hydroxy ***thiol*** esters. The molar equivalents of epoxidized unsaturated ester epoxidized groups can be calculated by the equation: ##EQU4##

DETD In this equation, EUES GMW is the average gram molecular weight of the epoxidized unsaturated ester, EUES Mass is the mass of the epoxidized unsaturated ester, and EUES ***Epoxide*** is the average number of ***epoxide*** groups per epoxidized unsaturated ester molecule. In some embodiments, the ***mercaptan*** to ***epoxide*** group molar ratio is greater than 0.2. In other embodiments, the ***mercaptan*** to ***epoxide*** group molar ratio is greater than 0.5; alternatively, greater than 1; or alternatively, greater than 2. In other embodiments, the hydrogen sulfide to ***epoxide*** group molar ratio ranges from 0.2 to 10; alternatively, from 0.5 to 8; alternatively, from 0.75 to 5; or alternatively, from 1 to 3.

DETD In some aspects, the reaction of the ***mercaptan*** and the epoxidized unsaturated ester occurs in the presence of a catalyst.

Generally, the catalyst is any catalyst that is capable of catalyzing the reaction of the ***mercaptan*** and the epoxidized unsaturated ester to produce the desired hydroxy ***thiol*** ester. In one aspect, the catalyst is selected from the group consisting of homogeneous and heterogeneous catalysts. In other aspects, the catalyst is selected from the group consisting of zeolites, heterogeneous catalysts, homogeneous catalysts, and mixtures thereof. In another aspect, the catalyst is an amine. In other aspects, the catalyst is selected from the group consisting of cyclic conjugated amines, 1,8-diazabicyclo[5.4.0]undec-7-ene, 1,5-diazabicyclo[4.3.0]non-5-ene, and mixtures thereof.

DETD In some aspects, the reaction of the ***mercaptan*** and the epoxidized unsaturated ester occurs in the presence of a catalyst.

Generally, the catalyst is any catalyst that is capable of

catalyzing the reaction of the ***mercaptan*** and the epoxidized unsaturated ester to produce the desired hydroxy ***thiol*** ester. In some embodiments the catalyst is an organic base. In some embodiments, the catalyst can be 1,8-diazabicyclo[5.4.0]undec-7-ene. (What other catalysts may be used?)

DETD The reaction of the ***mercaptan*** and the epoxidized unsaturated ester can occur in a batch reactor or a continuous reactor. Any of the batch or continuous reactors described herein can be used in this reaction. Other suitable reactors will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD The time required for the reaction of the ***mercaptan*** and the epoxidized unsaturated ester can be any reaction time required to form the described hydroxy sulfide-containing ester. Generally, the reaction time is at least 15 minutes. In some embodiments, the reaction time ranges from 15 minutes to 72 hours; alternatively, from 30 minutes to 48 hours; or alternatively, from 45 minutes to 36 hours.

DETD In some embodiments, the process to produce the hydroxy sulfide-containing ester further comprises a step to remove the residual ***mercaptan*** after reacting the ***mercaptan*** and the epoxidized unsaturated ester. In some embodiments the hydroxy sulfide-containing ester is vacuum stripped. In some embodiments, the hydroxy sulfide-containing ester is vacuum stripped at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the hydroxy sulfide-containing ester is sparged with an inert gas to remove the ***mercaptan***. In some embodiments, the hydroxy sulfide-containing ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged hydroxy sulfide-containing ester comprises less than 5 weight percent of the ***mercaptan***. In other embodiments, the stripped or sparged hydroxy sulfide-containing ester comprises less than 2 weight percent of the ***mercaptan***; alternatively,

less than 1 weight percent of the ***mercaptan*** ; or alternatively, less than 0.5 weight percent of the ***mercaptan*** .

DETD The reaction between the ***mercaptan*** and the epoxidized unsaturated ester can be performed at any reaction temperature capable of forming the hydroxy sulfide-containing ester. In some embodiments, the reaction temperature is greater than -20.degree. C. In other embodiments, the reaction temperature is greater than 0.degree. C. ; alternatively, greater than 20.degree. C.; alternatively, greater than 50.degree. C.; or alternatively, greater than 80.degree. C. In yet other embodiments, the reaction temperature ranges from -20.degree. C. to 200.degree. C.; alternatively, from 20.degree. C. to 170.degree. C.; or alternatively, from 80.degree. C. to 140.degree. C.

DETD The reaction between the ***mercaptan*** and the epoxidized unsaturated ester can be performed at any reaction pressure that maintains the ***mercaptan*** and the epoxidized unsaturated ester in a substantially liquid state. In some embodiments, the reaction pressure ranges from 0 psig to 2000 psig. In other embodiments, the reaction pressure ranges from 0 psig to 1000 psig; alternatively, from 0 psig to 500 psig; or alternatively, from 0 psig to 200 psig.

DETD In another aspect, the process to produce a hydroxy sulfide-containing ester produces a hydroxy sulfide-containing ester having an ***epoxide*** group to sulfide group molar ratio less than 2.

Other hydroxy sulfide-containing ester ***epoxide*** group to sulfide group molar ratios are described herein. (The next passage needs to be incorporated into the hydroxy ***thiol*** ester section along with the first sentence of this paragraph.) Alternatively, the hydroxy sulfide-containing ester ***epoxide*** group to ***thiol*** group molar ratio can be less than 1.5; alternatively, less than 1.0; alternatively, less than 0.5; alternatively, less than 0.25; or alternatively, less than 0.1. In other embodiments, the hydroxy sulfide-containing ester can be substantially free of ***epoxide*** groups.

DETD As an embodiment of the present invention, processes for producing a sulfonic acid-containing ester and for producing a sulfonate-containing ester are advantageously provided. Generally, the process for producing the sulfonic acid-containing ester comprises the steps of contacting a

thiol ester and an oxidizing agent and oxidizing at least one ***thiol*** group of the ***thiol*** ester to produce a sulfonic acid group. The process for producing the sulfonate-containing ester comprises the steps of contacting a sulfonic acid-containing ester with a base and forming a sulfonate-containing ester.

DETD In an embodiment, the process to prepare a sulfonic acid-containing ester comprises the steps of contacting the ***thiol*** ester and the oxidizing agent and oxidizing the ***thiol*** ester to produce the sulfonic acid-containing ester. Generally the oxidizing agent oxidizes at least one ***thiol*** group of the ***thiol*** ester to a sulfonate group. The process to produce the sulfonic acid-containing ester composition can be applied to any ***thiol*** ester described herein to prepare any sulfonic acid-containing ester described herein. In some embodiments, the ***thiol*** ester includes a hydroxy group. For example, the ***thiol*** ester can be any hydroxy ***thiol*** ester described herein. The oxidizing agent can be any oxidizing agent described herein.

DETD In some aspects, the oxidation of the ***thiol*** ester occurs in the presence of a solvent. In some aspects, the solvent is water.

DETD The oxidizing agent that is contacted with the ***thiol*** ester can be any oxidizing agent capable of oxidizing a ***thiol*** group to a sulfonic acid group. In some embodiments, the oxidizing agent is oxygen. In other embodiments, the oxidizing agent is chlorine. In other embodiments, the oxidizing agent is dimethyl sulfoxide. In yet other embodiments, the oxidizing agent is a combination of a hydrogen halide and a catalytic amount of a dialkyl sulfide, such as dimethyl sulfoxide.

Other suitable oxidizing agents will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD The oxidation of the ***thiol*** ester can be performed at any temperature capable of converting the ***thiol*** ester to a sulfonic acid-containing ester. In some embodiments, the ***thiol*** ester is oxidized a temperature greater than -20.degree. C. In other embodiments, the ***thiol*** ester is oxidized at a temperature greater than 0.degree. C.; alternatively, greater than 20.degree.

C.; or alternatively, greater than 50.degree. C.

DETD The time required for the oxidation of the ***thiol*** ester can be any time required to form the desired sulfonic acid-containing ester.

Generally, the time required for the oxidation of the ***thiol*** ester is at least 15 minutes; alternatively, at least 30 minutes; alternatively, at least 45 minutes; or alternatively, at least 1 hour.

In some embodiments, the time required for the oxidation of the ***thiol*** ester ranges from 15 minutes to 12 hours; alternatively, from 30 minutes to 6 hours; alternatively, from 45 minutes to 3 hours.

DETD The oxidation of the ***thiol*** ester can be performed at any pressure that maintains the ***thiol*** ester and the oxidation agent in the proper state, which is not always a liquid state, to oxidize the ***thiol*** ester to a sulfonic acid-containing ester.

For example, when the oxidation agent is chlorine, the chlorine can be in the gaseous state. In some embodiments, the oxidation of the ***thiol*** ester can be performed at a pressure ranging from 0 psig to 2000 psig. In other embodiments, the oxidation of the ***thiol*** ester can be performed at a pressure ranging from 0 to 1000 psig; or alternatively, 0 to 500 psig.

DETD The oxidation of the ***thiol*** ester can be performed in a batch reactor or a continuous reactor, as described herein.

Additionally, the process to produce the sulfonic acid-containing ester can comprise additional process steps as recognized by those skilled in the art.

DETD The formation of the sulfonate-containing ester can be performed at any temperature capable of converting the sulfonic acid group of the sulfonic acid-containing ester to a sulfonate group. In some embodiments, the sulfonate-containing ester is formed at a temperature greater than -20.degree. C. In other embodiments, the ***thiol*** ester is oxidized at a temperature greater than 0.degree. C.; alternatively, greater than 20.degree. C.; or alternatively, greater than 50.degree. C. In yet other embodiments, the ***thiol*** ester is oxidized at a temperature ranging from 0.degree. C. to 250.degree. C.; alternatively, from 0.degree. C. to 150.degree. C.; or alternatively, from 20.degree. C. to 100.degree. C.

DETD A preferred sulfur-containing vegetable oil is MVO available from

Chevron Phillips Chemical Co. under the tradename Polymercaptopan 358.

Polymercaptopan 358 is made by the free radical addition of hydrogen sulfide to the double bonds in soybean oil. Typically, Polymercaptopan 358 has a ***thiol*** sulfur content of 5 to 10% and equivalent weights of 640 to 320, respectively.

DETD Another preferred sulfur-containing vegetable oil useful as part of the isocyanate-reactive component is a MHVO such as mercapto-hydroxy soybean oil. As described herein, a preferred mercapto-hydroxy soybean oil is made by the free radical addition of hydrogen sulfide to epoxidized soybean oil. Typically, the mercapto and hydroxy functionalities are equal and the ***mercaptopan*** content is about 8.3% ***thiol*** sulfur. The equivalent weight of this material is 192, which includes both mercapto and hydroxy functionalities.

DETD Yet another preferred sulfur-containing vegetable oil useful as part of the isocyanate-reactive component is a CMVO such as sulfur cross-linked mercaptanized soybean oil. Sulfur cross-linked mercaptanized soybean oil is made by the addition of elemental sulfur to mercaptanized soybean oil. In this process, a portion of the ***mercaptopan*** groups are consumed as cross-linking sites for the sulfur. Typical sulfur cross-linked mercaptanized soybean oil products by Chevron Phillips Chemical Co. include Runs #22, 194, 195, 196 and 197 and have a ***thiol*** sulfur content ranging from about 8.0% to 1.4% and equivalent weights ranging from about 400 to about 2250, respectively.

DETD For epoxy polymer encapsulated CRF material made from sulfur-containing vegetable oil, it has been found that the use of a tertiary amine catalyst is highly preferred. The amount used is such to be sufficient to give the desired reaction rate for the production of the encapsulated slow release fertilizer product. A non-limiting example of a suitable amine catalyst is diazobicyclo[5,4,0]undecene also known as 1,8-diazabicyclo[5,4,0]undec-7-ene [CAS# ***6674-22-2***] or "DBU", which is preferably used in the range of about 0.1% to 0.5% by weight of the coating. Other suitable catalyst materials will be apparent to those of ordinary skill in the art.

DETD The preferred sulfur-containing vegetable oil to be used in

production of an epoxy polymer coated CRF material is MHVO such as mercapto-hydroxy soybean oil. One such material is mercapto-hydroxy soybean oil known as MHSO 566-84 produced by Chevron Phillips Chemical Co. This preferred material contains 8.33% ***thiol*** sulfur, with an equivalent weight of 384, based upon the ***mercaptan*** functionality. DETD The unsaturated ester used as a feedstock to produce the ***thiol*** ester compositions described herein can be described using a number of different methods. One method of describing the unsaturated ester feedstock is by the number of ester groups and the number of carbon-carbon double bonds that comprise each unsaturated ester oil molecule. Suitable unsaturated ester used as a feedstock to produce the ***thiol*** ester compositions described herein minimally comprise at least 1 ester group and at least 1 carbon-carbon double bond. However, beyond this requirement, the number of ester groups and carbon-carbon double bonds comprising the unsaturated esters are independent elements and can be varied independently of each other. Thus, the unsaturated esters can have any combination of the number of ester groups and the number of carbon-carbon double bonds described separately herein. Suitable, unsaturated esters can also contain additional functional groups such as alcohol, aldehyde, ketone, epoxy, ether, aromatic groups, and combinations thereof. As an example, the unsaturated esters can also comprise hydroxy groups. An example of an unsaturated ester that contains hydroxy groups is castor oil. Other suitable unsaturated esters will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD In yet another aspect, the polyol or mixture of polyols used to produce the unsaturated ***thiol*** ester has a molecular weight or average molecular weight less than 500. In other embodiments, the polyol or mixture of polyols have a molecular weight or average molecular weight less than 300; alternatively less than 200; alternatively, less than 150; or alternatively, less than 100.

DETD Specific carboxylic acids used as a component of the carboxylic acid composition used to produce the unsaturated ester oil can have from 3 to

30 carbon atoms per carboxylic acid molecule. In some embodiments the carboxylic acid is linear. In some embodiments the carboxylic acid is branched. In some embodiments the carboxylic acid is a mixture of linear and branched carboxylic acids. In some embodiments the carboxylic acid can also comprise additional functional groups including alcohols, aldehydes, ketones, and ***epoxides***, among others.

DETD Minimally, the epoxidized unsaturated ester comprises at least one ***epoxide*** group. In an embodiment the epoxidized unsaturated ester comprises at least 2 ***epoxide*** groups; alternatively, at least 3 ***epoxide*** groups; or alternatively, at least 4 ***epoxide***.

In other embodiments, the epoxidized unsaturated ester comprises from 2 to 9 ***epoxide*** groups; alternatively, from 2 to 4 ***epoxide*** groups; alternatively, from 3 to 8 ***epoxide*** groups; or alternatively, from 4 to 8 ***epoxide*** groups.

DETD In some embodiments, the unsaturated ester comprises a mixture of epoxidized unsaturated esters. In this aspect, the number of ***epoxide*** groups in the epoxidized unsaturated ester is best described as an average number of ***epoxide*** groups per epoxidized unsaturated ester molecule. In some embodiments, the epoxidized unsaturated esters have an average of at least 1.5 ***epoxide*** groups per epoxidized unsaturated ester molecule; alternatively, an average of at least 2.5 ***epoxide*** groups per epoxidized unsaturated ester molecule; or alternatively, an average of at least 3 ***epoxide*** groups per epoxidized unsaturated ester molecule. In other embodiments, the epoxidized unsaturated esters have average of from 1.5 to 9 ***epoxide*** groups per epoxidized unsaturated ester molecule; alternatively, an average of from 3 to 8 ***epoxide*** groups per epoxidized unsaturated ester molecule; alternatively, an average of from 2 to 4 ***epoxide*** groups per epoxidized unsaturated ester molecule; or alternatively, from 4 to 8 ***epoxide*** groups per epoxidized unsaturated ester molecule.

DETD The ***thiol*** composition can include an average of greater than 0 to about 4 ***epoxide*** groups per triglyceride. The ***thiol*** composition can also include an average of

greater than

1.5 to about 9 ***epoxide*** groups per triglyceride.

DETD ***Mercaptans***

DETD Within some embodiments, an unsaturated ester or an epoxidized unsaturated ester is contacted with ***mercaptan***. Within these

embodiments, the ***mercaptan*** can be any ***mercaptan*** comprising from 1 to 20 carbon atoms. Generally, the ***mercaptan***

can have the following structure: HS--R.sup.3 wherein R3 is a C1 to

C20 organyl groups or a C1 to C20 hydrocarbyl groups. In further embodiments the R3 can be a C2 to C10 organyl group or a C2 to C10

hydrocarbyl group. In some embodiments, the ***mercaptan*** composition comprises a solvent. In one aspect, the ***mercaptan***

composition comprises at least one other functional group.

DETD The at least one other functional group can be selected from several

different groups. For example, the at least one other functional group

is an alcohol group, a carboxylic alcohol group, a carboxylic ester

group, an amine group, a sulfide group, a ***thiol*** group,

a

methyl or ethyl ester of a carboxylic acid group, or combinations thereof. Other types of functional groups will be apparent to those of

skill in the art and are to be considered within the scope of the present invention.

DETD In some embodiments, the ***mercaptan*** is selected from the group

consisting of 3-mercaptopropyl-trimethoxysilane, 2-

mercaptopyridine,

4-mercaptopyridine, 2-mercaptopirimidine, mercaptopyruvic acid, mercaptosuccinic acid, 2-mercaptopicotinic acid, 6-

mercaptopicotinic

acid, 2-mercaptophenol, 4-mercaptophenol, 3-mercpto-1,2-

propanediol,

3-mercpto-1,2-propanediol, 3-mercpto-1-propanesulfonic acid, 1-mercpto-2-propanol, 3-mercpto-1-propanol, 2-mercaptopropionic acid,

3-mercaptopropionic acid, 2-mercaptopbenzyl alcohol,

3-mercpto-2-butanol, 4-mercpto-1-butanol, 2-

mercaptopethanesulfonic

acid, 2-mercptoethanol, 2-mercptoethyl ether, 2-mercptoethyl sulfide,

16-mercaptophexadecanoic acid, 6-mercpto-1-hexanol,

4'-mercptoacetanilide, mercaptoacetic acid, 2-mercaptopbenzoic acid,

3-mercaptopbenzoic acid, 4-mercaptopbenzoic acid, 2-

mercaptopthiazoline,

3-mercpto-1H-1,2,4-triazole, 11-mercaptopundecanoic acid,

11-mercpto-1-undecanol, or combinations thereof.

DETD In some embodiments, the ***mercaptan*** is selected from the group

consisting of beta-mercptoethanol, 2-mercaptophenol, 3-

mercaptophenol,

4-mercaptophenol, 1-mercpto-2-propanol, 1-mercpto-3-propanol,

mercaptoacetic acid, 2-mercaptopropionic acid, 3-mercaptopropionic acid, 2-mercaptopbenzoic acid, 3-mercaptopbenzoic acid, 4-mercaptopbenzoic acid, 2-mercaptopbenzylalcohol, 3-mercaptop-2-butanol, 4-mercaptop-1-butanol, 2-mercaptopethyl ether, 2-mercaptopethyl sulfide, 6-mercaptop-hexanol, 3-mercaptop-1,2-propanediol, mercaptosuccinic acid, and mixtures thereof.

In further embodiments, the ***mercantan*** is selected from the group consisting of beta-mercaptopethanol, 1-mercaptop-2-propanol, 1-mercaptop-3-propanol, 2-mercaptopbenzylalcohol, 3-mercaptop-2-butanol, 4-mercaptop-1-butanol, 6-mercaptop-hexanol, 3-mercaptop-1,2-propanediol, and mixtures thereof. In further embodiments, the ***mercantan*** is selected from the group consisting 2-mercaptophenol, 3-mercaptophenol, 4-mercaptophenol, and mixtures thereof. In yet further embodiments, the ***mercantan*** is selected from the group consisting mercaptoacetic acid, 2-mercaptopropionic acid, 3-mercaptopropionic acid, 2-mercaptopbenzoic acid, 3-mercaptopbenzoic acid, 4-mercaptopbenzoic acid, mercaptosuccinic acid, and mixtures thereof.

DETD Within some embodiments, the inventive compositions described herein are reacted with an isocyanate compound to produce a polythiourethane composition. The isocyanate may be any isocyanates capable of reacting with the ***thiol*** esters, hydroxy ***thiol*** esters, and a cross-linked ***thiol*** esters described herein to form a polyurethane composition. Generally, the isocyanate compound has at least two isocyanate groups.

DETD In order to quantitatively measure the ***thiol*** sulfur, the ***thiol*** sulfur analyses were conducted using silver nitrate titration in accordance with ASTM D3227, with the following modifications designed to minimize probe fouling by silver salts: the samples were diluted in a known mass of tetrahydrofuran. The silver nitrate concentration was 0.01 N standardized against potassium iodide.

DETD ***Thiol*** sulfur was analyzed by three different tests. The first test used was the modified ASTM D3227, which resulted in a ***thiol*** sulfur measurement of 4.64%. The second test used to measure the ***thiol*** sulfur was SLP-1204, which is a test developed by Chevron Phillips Chemical Company LLP. By using the SLP-1204 test, the

resulting ***thiol*** sulfur measurement was 4.28%. Lastly, the total sulfur was measured by combustion analysis, which resulted in a total sulfur measurement of 4.27%.

DETD Vegetable oil (42 kg) was charged to a 100-gallon holding vessel. The vessel was purged with nitrogen and returned to atmospheric pressure.

Hydrogen sulfide (174 kg) was charged to the holding vessel. The vessel temperature was controlled from 25-30.degree. C. while the pressure was typically maintained between 380-400 psig. The reactants were continuously rolled from the holding tank through a stainless steel tubular photochemical reactor containing a 7.5 KW Hanovia medium pressure mercury lamp contained within a quartz tube. Reactor temperature, pressure, and composition were monitored over the course of the reaction. The reaction time was dependent upon reaching a desired composition of ***thiol*** sulfur. Upon completion, the unreacted hydrogen sulfide was slowly vented from the system. Residual H₂S was removed at 100.degree. C. and reduced pressure while passing nitrogen through a nitrogen sparge tube. The product was drained from the bottom of the reactor into a clean drum. The ***thiol*** sulfur measurements were 11.0% when using the modified ASTM D3227, 8.74% when using SLP-1204, and the total sulfur was 11.21% when using combustion analysis (total sulfur).

DETD The resulting mercaptanized soybean oil was subjected to nitrogen sparging under reduced pressure at 100.degree. C. for a period of 4 hours to remove any residual hydrogen sulfide. The ***thiol*** sulfur measurements were 13.0% when using the modified ASTM D3227, 9.82% when using SLP-1204, and 11.69% when using combustion analysis.

DETD Table 1 provides the properties of the mercaptanized soybean oil produced in examples 1-3.

TABLE 1

Mercaptanized Soybean Oil Product Properties
Cyclic Sulfide to ***Thiol***
Thiol Sulfur.sup..dagger. Group

C.dbd.C	to ***Thiol*** groups	Molar Ratio	Molar Ratio
Example	(wt %)		
1	4.28	0.02	2.79
2	11.0	0.03	0.26
3	13.0	0.03	0.51

.sup..dagger. ***Thiol*** sulfur content determined by the modified ASTM D3227
 DETD Soybean oil was charged to a 1000 gallon stirred reactor.
 Hydrogen sulfide was then charged to the reactor. After the hydrogen sulfide was charged to the reactor, the stirrers and the UV lamps were turned on and the reaction allowed to build temperature and pressure as the reaction proceeded. The reaction was continued until a minimum ***thiol*** sulfur content of 8 weight percent was achieved. After reaction was completion, the excess hydrogen sulfide was flashed from the reactor.
 For runs 2-5, the mercaptanized soybean oil product underwent an additional hydrogen sulfide stripping step comprising stripping hydrogen sulfide from the product under vacuum, 50 mm Hg, at 250.degree. F. (only true for runs 2-5).
 DETD Table 3 provides the details of the analysis of the mercaptanized soybean oil producing in the five 1000 gallon reactor runs.

TABLE 3

1000 gallon reactor Mercaptanized Soybean Oil Product Properties				Side Chain
Run	Number	***Thiol*** Sulfur.sup..dagger. Group ***Thiol*** Groups	Cyclic Sulfide to Molar Ratio	***Thiol*** C.dbd.C groups
1	9.3	--	--	71.6
2	9.6	0.04	0.48	72.3
3	9.2	0.03	0.59	69.1
4	9.3	0.03	0.62	71.6
5	10.1	0.03	0.54	72.3

.sup..dagger. ***Thiol*** sulfur content determined by Raman spectroscopy

Mercaptanized Castor Bean Oil
 DETD The analytical properties of the two mercaptanized castor oil products are provide in Table 4.

TABLE 4

Mercaptanized Castor Oil Product Properties				Side Chain
Example	Containing ***Thiol*** Groups	Sulfur.sup..dagger. C.dbd.C to Molar Ratio	***Thiol*** groups	
1	6.4	0.52	64.1	

.sup..dagger. ***Thiol*** sulfur content determined by Raman spectroscopy

Mercaptohydroxy Soybean Oil Synthetic Procedure

DETD Epoxidized Soybean Oil (700 g, .about.0.7 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 4.7 g, 30.5 mmol) were charged to a 1-L Hastelloy C autoclave reactor that was pressure tested to 630 psig. Hydrogen sulfide (H_{sub.2}S, 132.0 g, 3.87 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.degree. C. with stirring for 8 hrs, during which time the reactor pressure decreased from a maximum of 351 psig to 219 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H_{sub.2}S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N_{sub.2} for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N_{sub.2} sparged under vacuum (<5 mmHg) at 130-140.degree. C. for 16 hrs to remove residual H_{sub.2}S. The resulting light yellow, viscous sticky oil had a ***thiol*** sulfur (titration by modified ASTM D3227) content of 7.53 wt. %, 2.5 SH/molecule, or 2.35 meq SH/g. Combustion analysis indicated C, 64.37%; H, 10.20%; N, <0.15%; and S, 9.51%.

DETD Epoxidized Soybean Oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged to a 1-L Hastelloy C autoclave reactor, and the vessel was pressure tested to 630 psig. Hydrogen sulfide (H_{sub.2}S, 204.0 g, 5.99 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 97.degree. C. with stirring for 14 hrs, during which time the reactor pressure decreased from a maximum of 509 psig to 229 psig. The stirrer was stopped and while still warm (90-95.degree. C.), excess H_{sub.2}S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N_{sub.2} for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N_{sub.2} sparged under vacuum (<5 mmHg) at 130-140.degree. C. for 16 hrs to remove residual H_{sub.2}S. The resulting light yellow, viscous sticky oil had a ***thiol*** sulfur (titration by modified ASTM D3227) content of 4.14

wt. %, 1.4 SH/molecule, or 1.29 meq SH/g. Combustion analysis indicated C, 65.18%; H, 10.17%; N, <0.15%; and S, 7.80%.

DETD Epoxidized Soybean Oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged to a 1-L Hastelloy C autoclave reactor, and the vessel was pressure tested to 630 psig. Hydrogen sulfide (H_{sub.2}S, 204.0 g, 5.99 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.degree. C. with stirring for 10 hrs, during which time the reactor pressure decreased from a maximum of 578 psig to 489 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H_{sub.2}S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N_{sub.2} for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N_{sub.2} sparged under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove residual H_{sub.2}S. The resulting light yellow, viscous sticky oil had a ***thiol*** sulfur (titration with modified ASTM D3227) content of 8.28 wt. %, 2.8 SH/molecule, or 2.58 meq SH/g. Combustion analysis indicated C, 65.24%; H, 9.52%; N, 0.18%; and S, 9.53%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged to a 1-L Hastelloy C autoclave reactor that was pressure tested to 630 psig. Hydrogen sulfide (H_{sub.2}S, 204.0 g, 5.99 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.degree. C. with stirring for 12 hrs, during which time the reactor pressure decreased from a maximum of 587 psig to 498 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H_{sub.2}S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N_{sub.2} for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N_{sub.2} sparged under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove residual H_{sub.2}S. The resulting light yellow, viscous sticky oil had a ***thiol*** sulfur (titration by modified ASTM D3227) content of 8.24 wt. %, 2.8 SH/molecule, or 2.57 meq SH/g. Combustion analysis indicated

C, 63.39%; H, 10.01%; N, <0.15%; and S, 8.76%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged to a 1-L Hastelloy C autoclave reactor, and the vessel was pressure tested to 630 psig. Hydrogen sulfide (H_{sub.2}S, 204.0 g, 5.99 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.degree. C. with stirring for 8 hrs, during which time the reactor pressure decreased from a maximum of 606 psig to 537 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H_{sub.2}S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N_{sub.2} for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N_{sub.2} sparged under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove residual H_{sub.2}S. The resulting light yellow, viscous sticky oil had a ***thiol*** sulfur (titration by modified ASTM D3227) content of 7.34 wt. %, 2.5 SH/molecule, or 2.29 meq SH/g. Combustion analysis indicated C, 64.47%; H, 10.18%; N, <0.15%; and S, 8.40%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged to a 1-L Hastelloy C autoclave reactor that was pressure tested to 630 psig. Hydrogen sulfide (H_{sub.2}S, 204.0 g, 5.99 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.degree. C. with stirring for 6 hrs, during which time the reactor pressure decreased from a maximum of 586 psig to 556 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H_{sub.2}S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N_{sub.2} for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N_{sub.2} sparged under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove residual H_{sub.2}S. The resulting light yellow, viscous sticky oil had a ***thiol*** sulfur (titration by modified ASTM D3227) content of 5.93 wt. %, 2.0 SH/molecule, or 1.85 meq SH/g. Combustion analysis indicated C, 65.26%; H, 10.19%; N, <0.15%; and S, 8.43%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and

1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged to a 1-L Hastelloy C autoclave reactor, and the vessel was pressure tested to 630 psig. Hydrogen sulfide (H_{sub}.2S, 204.0 g, 5.99 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.degree. C. with stirring for 4 hrs, during which time the reactor pressure decreased from a maximum of 595 psig to 554 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H_{sub}.2S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N_{sub}.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N_{sub}.2 sparged under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove residual H_{sub}.2S. The resulting light yellow, viscous sticky oil had a ***thiol*** sulfur (titration by modified ASTM D3227) content of 5.36 wt. %, 1.8 SH/molecule, or 1.67 meq SH/g. Combustion analysis indicated C, 65.67%; H, 10.17%; N, 0.34%; and S, 9.84%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged to a 1-L Hastelloy C autoclave reactor that was pressure tested to 630 psig. Hydrogen sulfide (H_{sub}.2S, 204.0 g, 5.99 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.degree. C. with stirring for 4 hrs, during which time the reactor pressure decreased from a maximum of 577 psig to 519 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H_{sub}.2S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N_{sub}.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N_{sub}.2 sparged under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove residual H_{sub}.2S. The resulting light yellow, viscous sticky oil had a ***thiol*** sulfur (titration with AgNO_{sub}.3) content of 5.85 wt. %, 2.0 SH/molecule, or 1.82 meq SH/g. Combustion analysis indicated C, 65.09%; H, 10.15%; N, 0.35%; and S, 10.63%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged

to a 1-L Hastelloy C autoclave reactor, and the vessel was pressure tested to 630 psig. Hydrogen sulfide (H₂S, 204.0 g, 5.99 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.°C. with stirring for 2 hrs, during which time the reactor pressure decreased from a maximum of 577 psig to 508 psig. The stirrer was stopped and while still warm (80-85.°C.), excess H₂S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N₂ for 1 hr and the reactor contents drained warm (80-85.°C.). The reaction product was N₂ sparged under vacuum (<5 mmHg) at 130-140.°C. for 16 hrs to remove residual H₂S. The resulting light yellow, viscous sticky oil had a ***thiol*** sulfur (titration by modified ASTM D3227) content of 5.07 wt. %, 1.7 SH/molecule, or 1.58 meq SH/g. Combustion analysis indicated C, 63.96%; H, 10.01%; N, 0.35%; and S, 11.22%.

DETD Table 5 provides the properties of the mercaptohydroxy soybean oil samples produced in Examples 1-10.

TABLE 5

Ex-	Reac-	Reac-	***Epoxides***			
			tion	tion	***Mercaptan***	groups
ample	Time	Temp	Sulfur	SH per	left per	
Epoxide	:SH					
sample	(hrs)	(°C.)	(wt. %)	sup.1	molecule.sup.2	
molecule.sup.3						
		Molar Ratio				
1	0	N/A	N/A	0	4.3	--
2	8	85	7.53	2.5	1.8	0.72
3	14	97	4.14	1.4	2.9	2.07
4	10	85	8.28	2.8	1.5	0.54
5	12	85	8.24	2.8	1.5	0.54
6	8	85	7.34	2.5	1.8	0.72
7	6	85	5.93	2.0	2.3	1.15
8	4	85	5.36	1.8	2.5	1.40
9	4	85	5.85	2.0	2.3	1.15
10	2	85	5.07	1.7	2.6	1.529

.sup.1Thiol sulfur was determined by silver nitrate oxidation using ASTM D 3227

.sup.2Determined by wt. % ***thiol*** sulfur

.sup.3Determined by subtracting the SH/molecule from the starting material

epoxide content

DETD Epoxidized soybean oil and the catalyst were charged to a 1-L

Hastelloy

C autoclave reactor, and the vessel was pressure tested to 1000 psig.

Hydrogen sulfide was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at temperature a set period of time with stirring for 12

hrs. During the reaction time the reactor pressure usually decreased. At

the end of the reaction time, the stirrer was stopped and excess H₂S was slowly vented while the reaction mixture was warm to a

low-pressure flare. The reactor vapor space was then swept with N₂ for 1 hr and the reactor contents drained. The reaction product was

N₂ sparged under vacuum (<50 mmHg) at 100° C. for 16 hrs to remove residual H₂S. Table 6 provides the reaction conditions used

to produce the mercaptohydroxy soybean oils for several runs and the

thiol Sulfur content of the mercaptohydroxy soybean oils produced.

TABLE 6

Mercaptohydroxy Soybean Oil Production Runs

Run (minutes)	Epoxidized Soybean Oil (g) (wt. %)	Temperature Time	Catalyst (g)	H ₂ S: H ₂ S: ***Epoxide***		
				Thiol (g)	Molar Ratio	Sulfur.sup.a (.degree. C.)
556-41.sup..dagger.	249.6		1.950	214.0	5.86	64
	728		5.69			
556-53.sup..dagger.	250.0		2.000	213.0	5.81	100
	370		9.04			
556-47.sup..dagger.	250.5		1.050	213.0	5.81	101
	720		10.47			
407-81D.sup..dagger.	500.0		4.200	255.0	3.49	85
	480		7.53			
407-86.sup..dagger.	600.0		5.000	204.0	2.07	85
	600		8.28			
556-79.sup..dagger-dbl.	250.0		2.600	214.0	5.83	100
	720		6.68			
556-80.sup..dagger-dbl.	251.0		5.000	214.0	5.81	100
	720		9.51			

.sup..dagger.Catalyst was DBU

.sup..dagger-dbl.catalyst was triethylamine (TEA)

.sup..aThiol sulfur measured by silver nitrate titration using modified ASTM D

3227

DETD Run number 407-86 was subjected to the sodium methoxide methanolysis

procedure and subsequently analyzed by GC/MS. The GS/MS analysis indicated that the product had ***epoxide*** group to ***thiol*** group molar ratio of approximately 0.14. The methanolysis data also indicated that an average of 80.4 percent of the product mercaptohydroxy soybean oil contained sulfur.

DETD Mercaptanized soybean oil (900.1 g; 10.92 wt. % ***thiol*** sulfur,) was charged to a three necked flask along with elemental sulfur pellets (9.6 g). The reaction mixture was heated to 120.degree. C. until sulfur dissolved and then cooled to 99.degree. C. Tributylamine (4.8 g) was charged to the reaction mixture with an addition funnel drop wise.

The reaction mixture was mixed at 90.degree. C. for 2 hrs. H.sub.2S evolution was observed. The reaction product (904.8 g) was sparged with N.sub.2 under vacuum at 110.degree. C. for 4 hrs to remove residual H.sub.2S. The final product was a light yellow oil with a ***thiol*** sulfur of 6.33 wt. % (by modified ASTM D3227). The elemental combustion analysis was 70.19%; C, 10.37%; H, and 11.21%; S.

DETD Mercaptanized soybean oil (900.0 g; 10.92 wt. % ***thiol*** sulfur,) was charged to a three necked flask along with elemental sulfur pellets (36.0 g). The reaction mixture was heated to 120.degree. C. until sulfur dissolved and then cooled to 100.degree. C.

Tributylamine (4.8 g) was charged to the reaction mixture with an addition funnel drop wise. The reaction mixture was mixed at 90.degree. C. for 36 hrs. H.sub.2S evolution was observed. The reaction product (825.6 g) was sparged with N.sub.2 under vacuum at 90.degree. C. for 36 hrs to remove residual H.sub.2S. The reaction product was then sparged with N.sub.2 under vacuum at 110.degree. C. for 3 hrs to remove residual H.sub.2S. The final product was a light yellow oil with a ***thiol*** sulfur of 2.36 wt. % (by modified ASTM D3227). The elemental combustion analysis was 68.90%; C, 11.07%; H, and 12.25%; S.

DETD Mercaptanized soybean oil (900.1 g; 10.92 wt. % ***thiol*** sulfur,) was charged to a three necked flask along with elemental sulfur pellets (18.0 g). The reaction mixture was heated to 125.degree. C. until sulfur dissolved and then cooled to 101.degree. C.

Tributylamine (4.8 g) was charged to the reaction mixture with an addition funnel drop wise. The reaction mixture was mixed at 90.degree. C. for 2 hrs.

H._{sub}2S evolution was observed. The reaction product (901.5 g) was sparged with N._{sub}2 under vacuum at 110.degree. C. for 4 hrs to remove residual H._{sub}2S. The final product was a light yellow oil with a ***thiol*** sulfur of 4.9 wt. % (by modified ASTM D3227). The elemental combustion analysis was 69.58%; C, 11.25%; H, and 11.31%; S.

DETD Mercaptanized soybean oil (900.2 g; 10.92 wt. % ***thiol*** sulfur,) was charged to a three necked flask along with elemental sulfur pellets (45.0 g). The reaction mixture was heated to 125.degree. C. until sulfur dissolved and then cooled to 100.degree. C.

Tributylamine (4.8 g) was charged to the reaction mixture with an addition funnel drop wise. The reaction mixture was mixed at 90.degree. C. for 2 hrs. H._{sub}2S evolution was observed. The reaction product (915.0 g) was sparged with N._{sub}2 under vacuum at 110.degree. C. for 4 hrs to remove residual H._{sub}2S. The final product was a light yellow oil with a ***thiol*** sulfur of 1.41 wt. % (by modified ASTM D3227).

The elemental combustion analysis was 68.35%; C, 10.98%; H, and 13.28%; S.

DETD Numerous polythiourethane compositions were prepared by reacting a ***thiol*** ester composition with a diisocyanate in the presence of a catalyst by using the processes described herein for preparing such polythiourethane compositions. The compositions were produced using the different variables of feedstocks, diisocyanates, stoichiometry, and catalysts shown in Table 8. Once every combination of variable was used, over 1200 compositions were produced. Each of the feedstocks were reacted with each of the diisocyanates at each of the stoichiometries with each of the catalysts listed to produce the 1200+ compositions. The stoichiometry was based upon a ***thiol*** ester composition (MSO, MHSO, CMSO, MCO) active hydrogen (***thiol*** and hydroxyl group) to diisocyanate equivalent ratio. For example, castor oil was reacted with toluene diisocyanate at a stoichiometric value of 1.25 while using Jeffol.RTM. A-480 as the catalyst. As another example, a ***thiol*** ester composition was reacted with methane diisocyanate at a stoichiometric value of 0.9 while using the DABCO catalyst.

DETD In the first MCO polythiourethane example, MCO was weighed into a

polyethylene beaker. To the MCO agent was added Luprinate at a ***thiol*** to isocyanate mole ratio of 0.95. To this reaction mixture was added dibutyl tin dilaurate (DBTDL) at a weight percent of 0.125 based upon the total weight of the ingredients. The three-component reaction mixture was then manually stirred with a wooden Popsicle stick.

The entire pre-polymer mixture was then poured into a mold for curing and cured using curing profile B. After the curing time was complete it was determined that the preparation produced a polythiourethane polymer.

DETD In the second MCO polythiourethane example, MCO was weighed into a polyethylene beaker. To the MCO agent was added Luprinate M20S at a ***thiol*** to isocyanate mole ratio of 1.00. To this reaction mixture was added dibutyl tin dilaurate (DBTDL) at a weight percent of 0.125 based upon the total weight of the ingredients. The three-component reaction mixture was then manually stirred with a wooden Popsicle stick.

The entire pre-polymer mixture was then poured into a mold for curing and cured using curing profile B. After the curing time was complete it was determined that the preparation produced a polythiourethane polymer.

DETD In the polythiourethane compositions, the feedstock ***thiol*** ester compositions that were used included MSO (mercaptanized soybean oil), MHSO (mercaptohydroxy soybean oil), CMSO (cross-linked mercaptanized soybean oil), castor oil, and MCO (mercaptanized caster oil). The diisocyanates that were used to produce these compositions included MDI (4,4'-methylenebis(phenyl) diisocyanate), HMDI (4,4'-methylenebis(cyclohexyl) diisocyanate, which is also known as hydrogenated MDI), TDI (tolylene 2,4-diisocyanate), HDI (1,6-diisocyanatohexane, which is also known as hexamethylene diisocyanate), and Luprinate.TM. M20S (which is an oligomerized form of MDI and is also referred to as polymeric MDI that is produced by BASF Corporation). The catalysts that were used included DABCO (diazabicyclooctane-di-tertiary amine), DBTDL (dibutyl tin dilaurate-organometallic catalyst), Jeffol.RTM. A-480 (which is a tertiary amine polyol produced by Huntsman Based Chemicals), and BDMA (benzylidimethylamine).

DETD B1: Mercaptanized soybean oil (an example of MVO discussed above)--Polymercaptan 358, available from Chevron Phillips Chemical Co.;

8.65% ***thiol*** sulfur; 370 equivalent weight; viscosity of 510.6 cSt @ 21.degree. C.;

DETD B2: Mercapto-hydroxy soybean oil (an examples of MHVO discussed above)--A mercapto-hydroxy soybean oil made by the free radical addition of hydrogen sulfide to epoxidized soybean oil; the mercapto and hydroxy functionalities are equal; 8.335% ***thiol*** sulfur; equivalent weight 192 (including both mercapto and hydroxy functionalities);

DETD B3: Sulfur cross-linked mercaptanized soybean oil (an example of CMVO discussed above)--A sulfur cross-linked mercaptanized soybean oil made by the addition of elemental sulfur to mercaptanized soybean oil; ***thiol*** sulfur content 6.33%; equivalent weight 506;

DETD B4: Sulfur cross-linked mercaptanized soybean oil (an example of CMVO discussed above)--A sulfur cross-linked mercaptanized soybean oil made by the addition of elemental sulfur to mercaptanized soybean oil; ***thiol*** sulfur content 7.64%; equivalent weight 419; cross-linkcross-link

DETD F2: Amine catalyst: 1,8-Diazabicyclo[5,4,0]undec-7-ene (DBU), CAS# ***6674-22-2*** .

DETD Analysis of the ***Thiol*** Containing Esters, Hydroxy ***Thiol*** Containing Esters and Cross-Linked ***Thiol*** Containing Ester

DETD Particular aspects of the ***thiol*** containing esters, hydroxy ***thiol*** containing esters, cross-linked ***thiol*** ester, unsaturated esters and epoxidized unsaturated esters are measured particular analytical techniques. ***Thiol*** sulfur values were obtained using a silver nitrate titration as described in ASTM D3227 or by Raman spectroscopy. Carbon-carbon double bond to ***thiol*** group molar ratio, cyclic sulfide to ***thiol*** group molar ratios were determined by .sup.13C NMR and/or GC analysis of the ***thiol*** containing ester or hydroxy ***thiol*** containing ester side chains.

DETD ***Thiol*** Sulfur Content by Raman Spectroscopy

DETD ***Thiol*** Sulfur content was measured by both silver nitrate titration, ASTM D3227, and/or Raman spectroscopy. The Raman spectroscopy method is practiced by measuring the Raman spectra of the ***thiol*** containing ester, hydroxy ***thiol*** containing ester, cross-linked ***thiol*** ester and comparing the spectra to calibration standards containing know ***thiol*** compounds having know amounts of ***thiol*** groups. Generally, the calibration standard ***thiol***

compound has a similar structure to the ***thiol*** containing esters analyzed.

DETD The ***thiol*** containing esters, hydroxy ***thiol*** containing esters and cross-linked ***thiol*** ester ***thiol*** content were determined by comparing the Raman spectra of the ***thiol*** containing esters, hydroxy ***thiol*** containing esters and cross-linked ***thiol*** ester to calibration standards prepared from mercaptanized methyl oleate diluted in soybean oil to known ***thiol*** sulfur contents. ***Thiol*** sulfur calibration standards were prepared using standards using various known concentration of mercaptanized methyl oleate diluted in soybean oil.

DETD Raman spectra of the calibration standards and the ***thiol*** containing esters, hydroxy ***thiol*** containing esters and cross-linked ***thiol*** ester were measured using a Kaiser Hololab 5000 Process Raman spectrometer, using a 785 nm laser.

Thiol containing esters, hydroxy ***thiol*** containing esters and cross-linked ***thiol*** ester samples and the ***thiol*** sulfur calibration standard Raman spectra were obtained by collecting four 10 second scans which were then processed using Holoreact software.

Thiol sulfur values for the ***thiol*** containing esters, hydroxy ***thiol*** containing esters and cross-linked ***thiol*** ester were then calculated using the ratio of the peak area values of the ***thiol*** SH peak (center: 2575 cm⁻¹; area 2500-2650 cm⁻¹), and the C.dbd.O peak (center--1745 cm⁻¹; area--1700-1800 cm⁻¹) and comparing them to the peak area values for the calibration standards and interpolating the containing esters, hydroxy ***thiol*** containing esters and cross-linked ***thiol*** ester ***thiol*** sulfur contents. Repeatability of the ***thiol*** sulfur values as measured by Raman spectroscopy have been shown to have a standard deviation of 0.05-0.1 and a % RSD of 0.6-1.5 using 5 samples having a % ***thiol*** sulfur content ranging from 3.1-10.6 weight percent as measured over a two month period.

DETD The Raman spectroscopy technique for determining the ***thiol*** sulfur content of a ***thiol*** containing ester, hydroxy ***thiol*** containing ester, and a cross-linked ***thiol***

containing ester has been illustrated using a ***thiol*** containing ester produced from soybean oil. However, one skilled in the art may adapt and apply the Raman spectroscopy technique for determining the ***thiol*** sulfur content of other ***thiol*** containing esters, hydroxy ***thiol*** containing esters, and a cross-linked ***thiol*** containing esters described herein. DEDT C.dbd.C to ***Thiol*** Group and Cyclic Sulfide Group to ***Thiol*** Group Molar Ratios by .sup.13C NMR DEDT Carbon-carbon double bond to ***thiol*** group molar ratio and cyclic sulfide group to ***thiol*** group molar ratios were determined by .sup.13C NMR. ***Thiol*** containing ester .sup.13C NMR spectra were obtained on a Varian Mercury INOVA400 NMR, a Varian Mercury Plus 300 NMR, or equivalent spectrometer (75.5 MHz .sup.13C NMR). Peak areas were determined for the cyclic sulfide carbon atoms, ***thiol*** group HS--C carbon atoms and carbon-carbon double bonds carbon atoms using the .sup.13C NMR regions indicated in the table below:

Functional Group	.sup.13C NMR Region	Number of Carbon Atoms/Group
Cyclic Sulfide Carbon Atoms	49-49.5 ppm	2
HS--C Carbon Atoms	40-41.5 ppm	1
C.dbd.C Carbon Atoms	120-140 ppm	2
DETD The ***thiol*** containing ester cyclic sulfide to ***thiol*** group molar ratio were calculated by dividing the cyclic sulfide carbon atoms .sup.13C NMR peak area by 2 (to account for the 2 carbon atoms per cyclic sulfide group) and dividing the resultant number by the ***thiol*** group HS--C carbon atoms .sup.13C NMR peak area.		
The ***thiol*** containing ester carbon-carbon double bond to ***thiol*** group molar ratio were calculated by dividing the C.dbd.C carbon atoms .sup.13C NMR peak area by 2 (to account for the 2 carbon atoms per carbon-carbon double bond) and dividing the result number by the ***thiol*** group HS--C carbon atoms .sup.13C NMR peak area		
Offset sample .sup.13C NMR's for soybean oil and a ***thiol*** containing ester produced from soybean oil using the disclosed process is provided as FIG. 1.		
DETD The NMR technique for analyzing the unsaturated ester and the		

thiol containing ester produced from an unsaturated ester have been illustrated using ¹³C NMR on soybean oil the ***thiol*** containing ester produced from soybean oil. However, one skilled in the art may adapt and apply either the ¹³C NMR or ¹H NMR technique to analyze the unsaturated esters and ***thiol*** containing ester produced from the unsaturated ester described herein.

DETD ***Epoxide*** Group to ***Thiol*** Group Molar Ratios by ¹³C or ¹H NMR

DETD The ***epoxide*** group to ***thiol*** group molar ratios were determined using ¹H or ¹³C NMR. Hydroxy ***thiol*** containing ester ¹H or ¹³C NMR spectra were obtained on a Varian Mercury INOVA400 NMR, a Varian Mercury Plus 300 NMR, or equivalent spectrometer (300 MHz ¹H NMR--75.5 MHz ¹³C NMR).

Peak areas were determined for the ***epoxide*** group and sulfide group using the ¹³C and or ¹H regions indicated in the table below:

Functional Group	¹ H NMR Region	¹³ C NMR Region	Number of Carbon Atoms/ Group	Number of Hydrogen Atoms/ Group
2 Group Carbon Atoms HS--C	2.75-3.2 ppm	53.6-56.6 ppm	2	
Carbon Atoms	3.2-4 ppm	40-41.5 ppm	1	1
DETD The hydroxy ***thiol*** containing ester ***epoxide*** group to				
	thiol group molar ratio were calculated by dividing the ***epoxide*** group carbon atoms ¹ H NMR peak area by 2			
(to	account for the 2 hydrogen atoms attached to the ***epoxide***			
group	carbon atoms) and dividing the result number by the ***thiol*** group HS--C carbon atom hydrogens ¹³ C NMR peak area. Similarly,			
the	hydroxy ***thiol*** containing ester ***epoxide*** group to			
peak	***thiol*** group molar ratio were calculated using ¹³ C NMR areas.			
DETD	The average number of ***epoxide*** group per epoxidized unsaturated ester molecule can be determined utilizing similar			

methods

utilizing either the carbonyl group carbon atom or the C--O ester group

carbon atoms .sup.13C NMR peak areas in conjunction with the ***epoxide*** group .sup.13C NMR peak area. Sample .sup.1H

NMR's epoxidized soybean oil and a ***thiol*** containing ester produced

from epoxidized soybean oil 1 are provided in FIG. 2.

DETD The NMR technique for analyzing the epoxidized unsaturated ester and

the ***thiol*** containing ester produced from an epoxidized unsaturated ester (a hydroxy ***thiol*** containing ester) has been

illustrated using .sup.1H NMR on epoxidized soybean oil the ***thiol*** containing ester produced from epoxidized soybean oil.

However, one skilled in the art may adapt and apply either the .sup.1H

NMR or .sup.13C NMR technique to analyze the epoxidized unsaturated

esters and ***thiol*** containing ester produced from the epoxidized unsaturated ester described herein.

DETD Analysis of Unsaturated Esters, Epoxidized Unsaturated Esters, ***Thiol*** Containing Esters, and Hydroxy ***Thiol***

Containing

Esters by Methanolysis

DETD Many properties of the unsaturated esters, epoxidized unsaturated

esters, ***thiol*** containing esters, and hydroxy

thiol

containing ester were and/or can be determined by converting the complex

ester molecules into their component polyols and carboxylic acid methyl

esters. The converted esters are then analyzed by gas chromatography

(GC) and/or gas chromatography/mass spectrometry (GCMS) to

determine the composition of the complex ester side chains. Properties that are or can

be determined by the methanolysis followed by GC or GC/MS of the carboxylic acid methyl esters include the number of side chain

that

contain ***thiol*** groups, the percent of ***thiol***

group sulfur, the number of (or average number) of double bonds per ester

molecule, the molecular weight distribution (or average molecular weight) of the ester side chains, the number of (or average number of)

epoxide groups per ester molecule, the cyclic sulfide

to

thiol group molar ratio, the carbon-carbon double bond

to

thiol group molar ratio, and the ***epoxide***

group to

thiol group molar ratio, among others.

DETD Depending upon the material being subjected to the methanolysis

procedure, there are two methanolysis procedures that were practiced upon the unsaturated ester, epoxidized esters, ***thiol*** containing ester, and hydroxy ***thiol*** containing esters described within the experimental section.

DETD Unsaturated esters and ***thiol*** containing ester produced from unsaturated ester were subjected to a hydrogen chloride based methanolysis procedure. In the hydrogen chloride methanolysis procedure, a 50 to 100 mg sample of the ***thiol*** containing ester is contacted with 3 mL of 3 N methanolic HCl and reacted for 2 hours a 50.degree. C. The solution is then allowed to cool and the neutralized with a dilute sodium bicarbonate solution. The solution's organic components are then extracted with ethyl ether and analyzed by GC and/or GC/MS. Additional details for the methanolic hydrogen chloride methanolysis procedure may be found in the product specification sheet for methanolic HCl, 0.5 N and 3 N as supplied by Supelco.

DETD Epoxidized unsaturated esters and hydroxy ***thiol*** containing esters produced from epoxidized unsaturated esters were subjected to a sodium methoxide based methanolysis procedure. The sodium methoxide methanolysis procedure was based upon the procedure disclosed in U.S. Pat. No. 3,991,089. In the sodium methoxide methanolysis procedure, approximately 1 g of the ester was placed in a 50 mL vial with 5.0 mL 25% sodium methoxide in methanol, and 10 mL methanol. The mixture was shaken for approximately 1 hour at room temperature, during which time the solution became one phase. The mixture was then poured into 25 mL of distilled water. Diethyl ether, 25 mL, was added to the solution and the mixture was acidified with 0.5 N HCl to a pH of approximately 5. The organic layer was separated from the aqueous layer using a separatory funnel. The organic layer was washed successively with distilled water (15 mL) and brine solution (15 mL) and then dried over magnesium sulfate. The magnesium sulfate was separated from the organic solution by filtration and the solvent removed by rotary evaporation.

DETD FIG. 3 provides a GC/MS trace of a mercaptanized soybean oil subjected to the methanolysis procedure and analyzed by GC/MS using a HP-30 30 .m.times.0.32 mm id.times.0.25 .mu.m film thickness GC Column.

Table 11 provides the GC/MS trace peak assignments.

TABLE 11

GC/MS Data for Methanolysis of A ***Thiol*** Containing Ester
Produced from
Soybean Oil
GC Retention time Methyl Ester Carboxylic Acid Assignment

21.58	Methyl hexadecanoate
23.66	Methyl (C18 monoene)oate
23.74	Methyl (C18 monoene)oate
23.96	Methyl octadecanoate
26.46	Methyl (C18 Monoene monomercaptan)oate
26.59	Methyl (C18 Monoene monomercaptan)oate
26.66	Methyl (C18 Monoene monomercaptan)oate
26.80	Methyl (C18 monomercaptan)oate
27.31	Methyl (C18 cyclic sulfide)oate
27.44	Methyl (C18 cyclic sulfide)oate
29.04	Methyl (C18 dimercaptan)oate
29.15	Methyl (C18 dimercaptan)oate
29.37	Methyl (C18 monoene dimercaptan)oate
29.46	Methyl (C18 monoene dimercaptan)oate
30.50	Methyl (C18 di (cyclic sulfide))oate

Peaks at 29.37 or 29.46 could also contain Methyl (C18 cyclic sulfide monomercaptan)oate isomers as part of those peaks.

DETD FIG. 5 provides a GC/MS trace of an epoxidized soybean oil contacted with hydrogen sulfide (a hydroxy ***thiol*** containing ester) subjected to the methanolysis procedure and analyzed by GC/MS using a HP-5 30 m.times.0.32 mm id.times.0.25 .mu.m film thickness GC Column.

Table 13 provides the GC/MS trace peak assignments.

TABLE 13

GC/MS Data for Methanolysis of a Hydroxy ***Thiol*** Containing Ester Produced from Epoxidized Soybean Oil
GC Retention time Methyl Ester Carboxylic Acid Assignment

16.09	Methyl hexadecanoate
17.68	Methyl octadecanoate
18.94	Methyl (C18 monoepoxide)oate
19.94	Methyl (C18 diepoxide)oate
20.14	Methyl (C18 diepoxide)oate
20.75	Methyl (C18 monohydroxy monothiol)oate
21-21.5	Methyl (C18 triepoxide)oate
22.82	Methyl (C18 dihydroxy dithiol)oate
22.90	Methyl (C18 monoepoxide monohydroxy monothiol)oate
27-27.5	Unidentified mixture of C18 sulfur containing methyl esters

DETD The methanolysis procedure and GC/MS procedure has been illustrate using soybean oil, epoxidized soybean oil, and the ***thiol*** containing products derived from soybean oil and epoxidized soybean oil.

However, one skilled in the art can easily adapt the procedures to the

analysis of other unsaturated esters, epoxidized unsaturated ester, and the ***thiol*** containing products derived from the unsaturated esters and epoxidized unsaturated esters as described herein. DETD The polythiourethane produced from the ***thiol*** containing esters, hydroxy ***thiol*** containing esters, and cross linked ***thiol*** containing ester were analyzed using ASTM E1545-95A and

E228-95 to provide the glass transition temperatures and the coefficients of thermal expansion. Shore hardness of the polythiourethanes were determined using ASTM D2240-02A. The polythiourethane were also subject to a subjective analysis classifying the polythiourethanes as hard, flexible, rubbery, rigid, tough, brittle, and other characteristics.

CLM What is claimed is:

1. A hydroxy ***thiol*** ester composition comprising hydroxy ***thiol*** ester molecules having an average of at least 1 ester average groups per hydroxy ***thiol*** ester molecule and having an average of at least 1 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule.

CLM What is claimed is:

2. The composition of claim 1, wherein the hydroxy ***thiol*** ester molecules have an average ranging from 1.5 to 9 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule.

CLM What is claimed is:

3. The composition of claim 1, wherein the hydroxy ***thiol*** ester molecules have an average of greater than 2.5 weight percent ***thiol*** sulfur.

CLM What is claimed is:

4. The composition of claim 1, wherein the hydroxy ***thiol*** ester molecules have an average ranging from 8 to 10 weight percent ***thiol*** sulfur.

CLM What is claimed is:

5. The composition of claim 1, wherein the hydroxy ***thiol*** ester molecules have a molar ratio of ***epoxide*** groups to the .alpha.-hydroxy ***thiol*** groups of less than 2.

CLM What is claimed is:

6. The composition of claim 1, wherein greater than 40 percent of the hydroxy ***thiol*** ester molecule total side chains contain sulfur.

CLM What is claimed is:

7. The composition of claim 1, wherein the composition is substantially free of ***epoxide*** groups.

CLM What is claimed is:
8. A hydroxy ***thiol*** ester composition comprising hydroxy ***thiol*** ester molecules having an average of at least 1 ester groups per hydroxy ***thiol*** ester molecule, having an average of at least 1 ***thiol*** groups per hydroxy ***thiol*** ester molecule, and having an average of at least 1 alcohol groups per hydroxy ***thiol*** ester molecule.

CLM What is claimed is:
9. The composition of claim 8, wherein the hydroxy ***thiol*** ester molecules have an average ranging from 1.5 to 9 ***thiol*** groups per hydroxy ***thiol*** ester molecule.

CLM What is claimed is:
10. The composition of claim 8, wherein the hydroxy ***thiol*** ester molecules have an average ranging from 1.5 to 9 alcohol groups per hydroxy ***thiol*** ester molecule.

CLM What is claimed is:
11. The composition of claim 8, wherein the hydroxy ***thiol*** ester molecules have an average of greater than 2.5 weight percent ***thiol*** sulfur.

CLM What is claimed is:
12. The composition of claim 8, wherein the hydroxy ***thiol*** ester molecules have an average ranging from 8 to 10 weight percent ***thiol*** sulfur.

CLM What is claimed is:
13. The composition of claim 8, wherein the hydroxy ***thiol*** ester molecules have a molar ratio of ***epoxide*** groups to ***thiol*** groups of less than 2.

CLM What is claimed is:
14. The composition of claim 8, wherein greater than 40 percent of the hydroxy ***thiol*** ester molecule total side chains contain sulfur.

CLM What is claimed is:
15. The composition of claim 8, wherein the composition is substantially free of ***epoxide*** groups.

CLM What is claimed is:
16. A process for preparing a hydroxy ***thiol*** ester composition,

comprising the steps of: a) contacting hydrogen sulfide and an epoxidized unsaturated ester composition comprising epoxidized unsaturated esters having an average of at least 1 ester groups per epoxidized unsaturated ester molecule and having an average of at least 1 ***epoxide*** groups per epoxidized unsaturated ester molecule; and b) reacting the hydrogen sulfide and the epoxidized unsaturated esters to form the hydroxy ***thiol*** ester composition.

CLM What is claimed is:
19. The process of claim 16, wherein a molar ratio of the hydrogen sulfide to ***epoxide*** groups in the epoxidized unsaturated esters is greater than 1.

CLM What is claimed is:
21. The process of claim 16, wherein the hydroxy ***thiol*** ester composition comprises hydroxy ***thiol*** ester molecules having an average of greater than 2.5 weight percent ***thiol*** sulfur.

CLM What is claimed is:
22. The process of claim 16, wherein the hydroxy ***thiol*** ester composition comprises hydroxy ***thiol*** ester molecules having an average ranging from 8 to 10 weight percent ***thiol*** sulfur.

CLM What is claimed is:
23. The process of claim 16, wherein the hydroxy ***thiol*** ester composition comprises hydroxy ***thiol*** ester molecules having greater than 40 percent of the hydroxy ***thiol*** ester molecule total side chains contain sulfur.

CLM What is claimed is:
24. A process for preparing a hydroxy ***thiol*** ester composition comprising the steps of: a) contacting a polyol composition and a hydroxy ***thiol*** carboxylic acid composition; and b) reacting the polyol composition and the hydroxy ***thiol*** carboxylic acid composition to produce the hydroxy ***thiol*** ester composition comprising hydroxy ***thiol*** ester molecules having an average of at least 1 ester groups per hydroxy ***thiol*** ester molecule and having an average of at least 1 .alpha.-hydroxy ***thiol***

groups per hydroxy ***thiol*** ester molecule.

IT 102-85-2, Tri-n-butylphosphite ***6674-22-2*** ,
1,8-Diazabicyclo[5.4.0]undec-7-ene
(activator; thiol ester compns. prep'd. by reacting H2S with
unsatd.
esters, such as soybean oil for manuf. monomers for prodn. of
polythiourethanes for fertilizers)

ACCESSION NUMBER: 2006:41458 USPATFULL <<LOGINID::20090306>>
TITLE: ***Thiol*** ester compositions and processes
for
making and using same

INVENTOR(S): Brown, Chad W., Bartlesville, OK, UNITED STATES
Refvik, Mitchell D., Bartlesville, OK, UNITED
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PATENT ASSIGNEE(S): Herron, Steven J., Kingwood, TX, UNITED STATES
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NUMBER OF CLAIMS:	24	
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CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L11 ANSWER 31 OF 85 USPATFULL on STN
SUMM The invention includes a process for the manufacturing of a
compound of
Formula I or its ester or salt thereof, ##STR2## wherein
Z.sup.1,
Z.sup.2, Z.sup.3, and Z.sup.4 are independently selected from the
group
consisting of hydrogen and alkyl, said alkyl optionally
substituted by
hydroxy, alkyl, alkenyl, acyl, nitro, amino, halo, carboxy and
cyano;
Z.sup.5 and Z.sup.6 are the same or different and independently
selected from
the group consisting of alkyl, alkenyl, and aryl all of which can
be
optionally substituted by hydroxy, alkyl, alkenyl, acyl, nitro,
amino,

halo, carboxy and cyano;
Z.sup.5 and Z.sup.6 can come together to form a carbocyclic ring;
M is selected from the group consisting of hydrogen, an optionally substituted unsaturated alkyl having from 1 to 10 carbon atoms, and an optionally substituted saturated alkyl having from 1 to 10 carbon atoms, said optionally substituted unsaturated alkyl and optionally substituted saturated alkyl optionally containing a polar or charged functionality;
or M is selected from the group consisting of hydrogen, an optionally substituted unsaturated acyl having from 1 to 18 carbon atoms, and an optionally substituted saturated acyl having from 1 to 18 carbon atoms, said optionally substituted unsaturated acyl and optionally substituted saturated acyl optionally containing a polar or charged functionality;
J is selected from the group consisting of an optionally substituted unsaturated alkyl having from 1 to 10 carbon atoms, and an optionally substituted saturated alkyl having from 1 to 10 carbon atoms, said optionally substituted unsaturated alkyl and optionally substituted saturated alkyl optionally containing a polar or charged functionality;
or J is selected from the group consisting of an optionally substituted unsaturated acyl having from 1 to 18 carbon atoms and an optionally substituted saturated acyl having from 1 to 18 carbon atoms, said optionally substituted unsaturated acyl and optionally substituted saturated acyl optionally containing a polar or charged functionality;
the process comprising:
reacting a compound of Formula II, ##STR3## wherein Z.sup.1, Z.sup.2, Z.sup.3, Z.sup.4, Z.sup.5 and Z.sup.6 are as previously defined, with a compound of Formula III, ##STR4## wherein Y is R.sup.2 or NR.sup.2R.sup.5;
R.sup.1, R.sup.2, R.sup.3 and R.sup.4 and R.sup.5 are independently selected from an optionally substituted C.sub.1-C.sub.10 alkyl or an optionally substituted C.sub.2-C.sub.10 alkenyl;
R.sup.1 and R.sup.2 can optionally come together to form a ring; R.sup.3 and R.sup.4 can optionally come together to form a ring; and a compound selected from the group consisting of a saturated or unsaturated acyl halide, saturated or unsaturated carboxylic acid anhydride and a saturated or unsaturated activated carboxylic acid ester, all of which may optionally be substituted by one or more substituents selected from the group consisting of protected hydroxy,

alkyl, alkenyl, acyl, nitro, protected amino, amino, halo, protected carboxy and cyano; or, a compound selected the group consisting of a saturated or unsaturated alkyl halide, saturated or unsaturated alkyl-O-sulfonyl alkyl, a saturated or unsaturated alkyl-O-sulfonyl aryl, a saturated or unsaturated alkyl-O-acyl, and a saturated or unsaturated ***epoxide***, all of which may optionally be substituted by one or more substituents selected from the group consisting of protected hydroxy, alkyl, alkenyl, acyl, nitro, protected amino, halo, protected carboxy, ***epoxide*** and cyano; and, separating and isolating the compound of Formula I.

SUMM The terms "alkyl" or "alk", alone or in combination, unless otherwise specified, means a saturated straight or branched primary, secondary, or tertiary hydrocarbon from 1 to 16 carbon atoms, including, but not limited to methyl, ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl, and sec-butyl. The alkyl group may be optionally substituted where possible with any moiety that does not otherwise interfere with the reaction or that provides an improvement in the process, including but not limited to halo, haloalkyl, hydroxyl, carboxyl, acyl, aryl, acyloxy, amino, amido, carboxyl derivatives, alkylamino, dialkylamino, arylamino, alkoxy, aryloxy, nitro, cyano, sulfonic acid, ***thiol***, imine, sulfonyl, sulfanyl, sulfinyl, sulfamonyl, ester, carboxylic acid, amide, phosphonyl, phosphinyl, phosphoryl, phosphine, thioester, thioether, acid halide, anhydride, oxime, hydrozine, carbamate, phosphonic acid, phosphonate, either unprotected, or protected as necessary, as known to those skilled in the art.

SUMM The term "alkenyl", alone or in combination, means a non-cyclic alkyl of 2 to 10 carbon atoms having one or more unsaturated carbon-carbon bonds. The alkenyl group may be optionally substituted where possible with any moiety that does not otherwise interfere with the reaction or that provides an improvement in the process, including but not limited to halo, haloalkyl, hydroxyl, carboxyl, acyl, aryl, acyloxy, amino, amido, carboxyl derivatives, alkylamino, dialkylamino, arylamino, alkoxy, aryloxy, nitro, cyano, sulfonic acid, ***thiol***, imine,

sulfonyl, sulfanyl, sulfinyl, sulfamonyl, ester, carboxylic acid, amide, phosphonyl, phosphinyl, phosphoryl, phosphine, thioester, thioether, acid halide, anhydride, oxime, hydrozine, carbamate, phosphonic acid, phosphonate, either unprotected, or protected as necessary, as known to those skilled in the art.

SUMM The term "alkynyl", alone or in combination, means a non-cyclic alkyl of 2 to 10 carbon atoms having one or more triple carbon-carbon bonds, including but not limited to ethynyl and propynyl. The alkynyl group may be optionally substituted where possible with any moiety that does not otherwise interfere with the reaction or that provides an improvement in the process, including but not limited to halo, haloalkyl, hydroxyl, carboxyl, acyl, aryl, acyloxy, amino, amido, carboxyl derivatives, alkylamino, dialkylamino, arylamino, alkoxy, aryloxy, nitro, cyano, sulfonic acid, ***thiol***, imine, sulfonyl, sulfanyl, sulfinyl, sulfamonyl, ester, carboxylic acid, amide, phosphonyl, phosphinyl, phosphoryl, phosphine, thioester, thioether, acid halide, anhydride, oxime, hydrozine, carbamate, phosphonic acid, phosphonate, either unprotected, or protected as necessary, as known to those skilled in the art.

SUMM The term "aryl", alone or in combination, means a carbocyclic aromatic system containing one, two or three rings wherein such rings may be attached together in a pendent manner or may be fused. The "aryl" group can be optionally substituted where possible with one or more of the moieties selected from the group consisting of alkyl, alkenyl, alkynyl, heteroaryl, heterocyclic, carbocycle, alkoxy, oxo, aryloxy, arylalkoxy, cycloalkyl, tetrazolyl, heteroaryloxy; heteroarylalkoxy, carbohydrate, amino acid, amino acid esters, amino acid amides, alditol, halogen, haloalkylthi, haloalkoxy, haloalkyl, hydroxyl, carboxyl, acyl, acyloxy, amino, aminoalkyl, aminoacyl, amido, alkylamino, dialkylamino, arylamino, nitro, cyano, ***thiol***, imide, sulfonic acid, sulfate, sulfonate, sulfonyl, alkylsulfonyl, aminosulfonyl, alkylsulfonylamino,

haloalkylsulfonyl, sulfanyl, sulfinyl, sulfamoyl, carboxylic ester, carboxylic acid, amide, phosphonyl, phosphinyl, phosphoryl, thioester, thioether, oxime, hydrazine, carbamate, phosphonic acid, phosphate, phosphonate, phosphinate, sulfonamido, carboxamido, hydroxamic acid, sulfonylimide or any other desired functional group that does not inhibit the pharmacological activity of this compound, either unprotected, or protected as necessary, as known to those skilled in the art. In addition, adjacent groups on an "aryl" ring may combine to form a 5- to 7-membered saturated or partially unsaturated carbocyclic, aryl, heteroaryl or heterocyclic ring, which in turn may be substituted as above.

SUMM The term "substituted", means that one or more hydrogen on the designated atom or substituent is replaced with a selection from the indicated group, provided that the designated atom's normal valency is not exceeded, and the that the substitution results in a stable compound. When a substituent is "oxo" (keto) (i.e., .dbd.O), then 2 hydrogens on the atom are replaced. If the term is used without an indicating group, an appropriate substituent known by those skilled in art may be substituted, including, but not limited to, hydroxyl, alkyl, alkenyl, acyl, nitro, protected amino, halo, protected carboxy, ***epoxide***, and cyano.

SUMM The term "polar or charged functionality" means a polar or charged group attached in place of one or more hydrogen atoms. Non limiting examples include carboxy, hydroxy, amino, ***epoxide***, etc.

SUMM The term " ***epoxide*** " means the radical ##STR7## wherein all R groups are independently selected from hydrogen, alkyl, aryl and arylalkyl wherein said alkyl, aryl and arylalkyl may optionally be substituted with a polar functionality.

DETD In a broad description, the invention encompasses the method of manufacturing a compound of Formula I or its ester or salt thereof, ##STR13## wherein Z.sup.1, Z.sup.2, Z.sup.3, and Z.sup.4 are independently selected from the group consisting of hydrogen and alkyl, said alkyl optionally substituted by hydroxy, alkyl, alkenyl, acyl,

nitro, amino, halo, carboxy and cyano;
Z.sup.5 and Z.sup.6 are the same or different and independently selected from
the group consisting of alkyl, alkenyl, and aryl all of which can be
optionally substituted by hydroxy, alkyl, alkenyl, acyl, nitro, amino, halo, carboxy and cyano;
Z.sup.5 and Z.sup.6 can come together to form a carbocyclic ring;
M is selected from the group consisting of hydrogen, an optionally substituted unsaturated alkyl having from 1 to 10 carbon atoms, and an optionally substituted saturated alkyl having from 1 to 10 carbon atoms, said
optionally substituted unsaturated alkyl and optionally substituted
saturated alkyl optionally containing a polar or charged functionality;
or M is selected from the group consisting of hydrogen, an optionally substituted unsaturated acyl having from 1 to 18 carbon atoms, and an
optionally substituted saturated acyl having from 1 to 18 carbon atoms, said
optionally substituted unsaturated acyl and optionally substituted
saturated acyl optionally containing a polar or charged functionality;
J is selected from the group consisting of an optionally substituted unsaturated alkyl having from 1 to 10 carbon atoms, and an
optionally substituted saturated alkyl having from 1 to 10 carbon atoms, said
optionally substituted unsaturated alkyl and optionally substituted
saturated alkyl optionally containing a polar or charged functionality;
or J is selected from the group consisting of an optionally substituted unsaturated acyl having from 1 to 18 carbon atoms and an
optionally substituted saturated acyl having from 1 to 18 carbon atoms, said
optionally substituted unsaturated acyl and optionally substituted
saturated acyl optionally containing a polar or charged functionality;
the process comprising:
reacting a compound of Formula II, ##STR14## wherein Z.sup.1,
Z.sup.2,
Z.sup.3, Z.sup.4, Z.sup.5 and Z.sup.6 are as previously defined,
with a
compound of Formula III, ##STR15## wherein Y is R.sup.2 or
NR.sup.2R.sup.5;
R.sup.1, R.sup.2, R.sup.3 and R.sup.4 and R.sup.5 are independently selected
from an optionally substituted C.sub.1-C.sub.10 alkyl or an
optionally substituted C.sub.2-C.sub.10 alkenyl;
R.sup.1 and R.sup.2 can optionally come together to form a ring;
R.sup.3 and R.sup.4 can optionally come together to form a ring; and
a

compound selected from the group consisting of a saturated or unsaturated acyl halide, saturated or unsaturated carboxylic acid anhydride and a saturated or unsaturated activated carboxylic acid ester, all of which may optionally be substituted by one or more selected from the group consisting of protected hydroxy, alkyl, alkenyl, acyl, nitro, protected amino, amino, halo, protected carboxy and cyano;

or a compound selected the group consisting of a saturated or unsaturated alkyl halide, saturated or unsaturated alkyl-O-sulfonyl alkyl, a saturated or unsaturated alkyl-O-acyl, and a saturated or unsaturated ***epoxide***, all of which may optionally be substituted by one or more selected from the group consisting of protected hydroxy, alkyl, alkenyl, acyl, nitro, protected amino, halo, protected carboxy, ***epoxide*** and cyano; and separating and isolating said compound of Formula I.

DETD In a 2.sup.nd embodiment, the invention is represented by the process to manufacture a compound of Formula I or its ester or salt thereof,

##STR16## wherein Z.sup.1, Z.sup.2, Z.sup.3, and Z.sup.4 are independently selected from the group consisting of hydrogen and alkyl, said alkyl optionally substituted by hydroxy, alkyl, alkenyl, acyl, nitro, amino, halo, carboxy and cyano;

Z.sup.5 and Z.sup.6 are the same or different and independently selected from the group consisting of alkyl, alkenyl, and aryl all of which can be optionally substituted by hydroxy, alkyl, alkenyl, acyl, nitro, amino, halo, carboxy and cyano;

Z.sup.5 and Z.sup.6 can come together to form a carbocyclic ring; M is selected from the group consisting of hydrogen, an optionally substituted unsaturated alkyl having from 1 to 10 carbon atoms, and an optionally substituted saturated alkyl having from 1 to 10 carbon atoms, said optionally substituted unsaturated alkyl and optionally substituted saturated alkyl optionally containing a polar or charged functionality;

and

J is selected from the group consisting of an optionally substituted unsaturated alkyl having from 1 to 10 carbon atoms, and an optionally substituted saturated alkyl having from 1 to 10 carbon atoms, said optionally substituted unsaturated alkyl and optionally substituted

saturated alkyl optionally containing a polar or charged functionality;
the process comprising:
reacting a compound of Formula II, ##STR17## wherein Z.sup.1, Z.sup.2,
Z.sup.3, Z.sup.4, Z.sup.5 and Z.sup.6 are as previously defined, with a compound of Formula III, ##STR18## wherein Y is R.sup.2 or NR.sup.2R.sup.5;
R.sup.1, R.sup.2, R.sup.3 and R.sup.4 and R.sup.5 are independently selected
from an optionally substituted C.sub.1-C.sub.10 alkyl or an optionally substituted C.sub.2-C.sub.10 alkenyl;
R.sup.1 and R.sup.2 can optionally come together to form a ring; R.sup.3 and R.sup.4 can optionally come together to form a ring; and a compound selected the group consisting of a saturated or unsaturated alkyl halide, saturated or unsaturated alkyl-O-sulfonyl alkyl, a saturated or unsaturated alkyl-O-sulfonyl aryl, a saturated or unsaturated alkyl-O-acyl, and a saturated or unsaturated ***epoxide***, all of which may optionally be substituted by one or more selected from the group consisting of protected hydroxy, alkyl, alkenyl, acyl, nitro, protected amino, halo, protected carboxy, ***epoxide*** and cyano; and separating and isolating said compound of Formula I.

DETD In a 3.sup.rd embodiment, the invention is represented by the process to manufacture a compound of Formula IV or its ester or salt thereof, ##STR19## wherein J is selected from the group consisting of an optionally substituted unsaturated alkyl having from 1 to 10 carbon atoms, and an optionally substituted saturated alkyl having from 1 to 10 carbon atoms, said optionally substituted unsaturated alkyl and optionally substituted saturated alkyl optionally containing a polar or charged functionality;

the process comprising:
reacting a compound of Formula V, ##STR20## with a compound of Formula III, ##STR21## wherein Y is R.sup.2 or NR.sup.2R.sup.5;
R.sup.1, R.sup.2, R.sup.3 and R.sup.4 and R.sup.5 are independently selected
from an optionally substituted C.sub.1-C.sub.10 alkyl or an optionally substituted C.sub.2-C.sub.10 alkenyl;
R.sup.1 and R.sup.2 can optionally come together to form a ring; R.sup.3 and R.sup.4 can optionally come together to form a ring; and a compound selected from the group consisting of a saturated or unsaturated alkyl halide, saturated or unsaturated alkyl-O-sulfonyl alkyl, a saturated or unsaturated alkyl-O-sulfonyl aryl, a

saturated or
unsaturated alkyl-O-acyl, and a saturated or unsaturated
epoxide
, all of which may optionally be substituted by one or more
substituents
selected from the group consisting of protected hydroxy, alkyl,
alkenyl,
acyl, nitro, protected amino, halo, protected carboxy,
epoxide
and cyano; and separating and isolating said compound of Formula
IV.

CLM What is claimed is:

10. A process for manufacturing a compound of Formula I or its
ester or
salt thereof, ##STR77## wherein Z.sup.1, Z.sup.2, Z.sup.3,
and
Z.sup.4 are independently selected from the group consisting of
hydrogen
and alkyl, said alkyl optionally substituted by hydroxy, alkyl,
alkenyl,
acyl, nitro, amino, halo, carboxy and cyano; Z.sup.5 and Z.sup.6
are
the same or different and independently selected from the group
consisting of alkyl, alkenyl, and aryl all of which can be
optionally
substituted by hydroxy, alkyl, alkenyl, acyl, nitro, amino, halo,
carboxy and cyano; Z.sup.5 and Z.sup.6 can come together to form
a
carbocyclic ring; M is selected from the group consisting of
hydrogen,
an optionally substituted unsaturated alkyl having from 1 to 10
carbon
atoms, and an optionally substituted saturated alkyl having from
1 to 10
carbon atoms, said optionally substituted unsaturated alkyl and
optionally substituted saturated alkyl optionally containing a
polar or
charged functionality; and J is selected from the group
consisting of
an optionally substituted unsaturated alkyl having from 1 to 10
carbon
atoms, and an optionally substituted saturated alkyl having from
1 to 10
carbon atoms, said optionally substituted unsaturated alkyl and
optionally substituted saturated alkyl optionally containing a
polar or
charged functionality; the process comprising: reacting a
compound of
Formula II ##STR78## wherein Z.sup.1, Z.sup.2, Z.sup.3,
Z.sup.4,
Z.sup.5 and Z.sup.6 are as previously defined, with a compound
of
Formula III, ##STR79## wherein Y is R.sup.2 or
NR.sup.2R.sup.5;
R.sup.1, R.sup.2, R.sup.3 and R.sup.4 and R.sup.5 are
independently
selected from an optionally substituted C.sub.1-C.sub.10 alkyl or
an
optionally substituted C.sub.2-C.sub.10 alkenyl; R.sup.1 and
R.sup.2

can optionally come together to form a ring; R.sup.3 and R.sup.4 optionally come together to form a ring; and a compound selected from the group consisting of a saturated or unsaturated alkyl halide, saturated or unsaturated alkyl-O-sulfonyl alkyl, a saturated or unsaturated alkyl-O-sulfonyl aryl, a saturated or unsaturated alkyl-O-acyl, and a saturated or unsaturated ***epoxide***, all of which may optionally be substituted by one or more substituents selected from the group consisting of protected hydroxy, alkyl, alkenyl, acyl, nitro, protected amino, halo, protected carboxy, ***epoxide*** and cyano; and separating and isolating the compound of Formula I.

CLM What is claimed is:
11. The process of claim 10 to manufacture a compound of Formula IV or its ester or salt thereof, ##STR80## wherein J is selected from the group consisting of an optionally substituted unsaturated alkyl having from 1 to 10 carbon atoms, and an optionally substituted saturated alkyl having from 1 to 10 carbon atoms, said optionally substituted unsaturated alkyl and optionally substituted saturated alkyl optionally containing a polar or charged functionality; the process comprising:
reacting a compound of Formula V ##STR81## with a compound of Formula III, ##STR82## wherein Y is R.sup.2 or NR.sup.2R.sup.5; R.sup.1, R.sup.2, R.sup.3 and R.sup.4 and R.sup.5 are independently selected from an optionally substituted C.sub.1-C.sub.10 alkyl or an optionally substituted C.sub.2-C.sub.10 alkenyl; R.sup.1 and R.sup.2 can optionally come together to form a ring; R.sup.3 and R.sup.4 can optionally come together to form a ring; and a compound selected from the group consisting of a saturated or unsaturated alkyl halide, saturated or unsaturated alkyl-O-sulfonyl alkyl, a saturated or unsaturated alkyl-O-sulfonyl aryl, a saturated or unsaturated alkyl-O-acyl, and a saturated or unsaturated ***epoxide***, all of which may optionally be substituted by one or more substituents selected from the group consisting of protected hydroxy, alkyl, alkenyl, acyl, nitro, protected amino, halo, protected carboxy, ***epoxide*** and cyano; and separating and isolating the compound of Formula IV.

IT ***3001-72-7***, Dbn ***6674-22-2***, Dbu

(prepn. of esters of probucol and derivs. thereof using acid anhydrides
in the presence of DBU or DBN)
ACCESSION NUMBER: 2005:306544 USPATFULL <<LOGINID::20090306>>
TITLE: Process of preparing esters and ethers of
probucol and
derivatives thereof
INVENTOR(S): Weingarten, M. David, Cumming, GA, UNITED STATES

	NUMBER	KIND	DATE
PATENT INFORMATION:	US 20050267187	A1	20051201
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NUMBER OF CLAIMS:	11	
EXEMPLARY CLAIM:	1	
LINE COUNT:	1405	
CAS INDEXING IS AVAILABLE FOR THIS PATENT.		

L11 ANSWER 36 OF 85 USPATFULL on STN
TI ***Thiol*** ester compositions and processes for making and
using
 same
AB ***Thiol*** ester compositions, methods of making the
thiol
 ester compositions, and methods of using the ***thiol***
ester
 compositions are provided. In some embodiments, the ***thiol***
ester compositions include ***thiol*** esters, hydroxy
thiol
 esters and cross-linked ***thiol*** esters. The ***thiol***
ester composition can be used to produce cross-linked
thiol
 esters, sulfonic acid-containing esters, sulfonate containing
esters and
thioacrylate containing esters. The ***thiol*** ester
compositions
 can be used to produce polythiourethanes. The polythiourethanes
can be
 used in fertilizers and fertilizer coatings.
SUMM The invention relates to ***thiol*** containing ester
compositions
 generally made from a reaction of unsaturated ester compositions
and a
 material capable of forming a ***thiol*** group. The
invention also
 relates to the processes for preparing such ***thiol***
containing
 compositions and uses for the ***thiol*** containing
compositions.

SUMM The present invention advantageously provides ***thiol*** containing compositions and methods of making such compositions.

In addition to the compositions and methods of making such compositions, products that include such compositions are also provided.

SUMM As an embodiment of the present invention, a ***thiol*** ester composition is advantageously provided. In this embodiment, the ***thiol*** ester composition includes ***thiol*** ester molecules that have an average of at least 1.5 ester groups per ***thiol*** ester molecule. The ***thiol*** ester molecules also have an average of at least 1.5 ***thiol*** groups per ***thiol*** ester molecule. The ***thiol*** ester molecules also have a molar ratio of cyclic sulfides to ***thiol*** groups of less than 1.5.

SUMM In some aspects, the ***thiol*** ester molecules have a molar ratio of cyclic sulfides to ***thiol*** groups ranging from 0 to 1.0. In some aspects, the ***thiol*** ester molecules have an average ranging from 1.5 to 9 ***thiol*** groups per ***thiol*** ester molecule. In some embodiments, the ***thiol*** ester molecules have a molar ratio of carbon-carbon double bonds to ***thiol*** groups of less than 1.5.

SUMM The amount of ***thiol*** sulfur or ***mercaptan*** sulfur contained within the ***thiol*** ester molecules can also vary. For example, in some embodiments, the ***thiol*** ester molecules have an average of greater than 5 weight percent ***thiol*** sulfur. In other embodiments, the ***thiol*** ester molecules have an average ranging from 8 to 10 weight percent ***thiol*** sulfur. In some embodiments, the ***thiol*** ester molecules have an average of less than 30 mole percent sulfur, which is present as cyclic sulfides. Alternatively, the ***thiol*** ester molecules have an average of less than 2 mole percent sulfur present as cyclic sulfides.

SUMM In some embodiments, the ***thiol*** ester molecules are produced from unsaturated esters that have an average of less than 25 weight percent of side chains that include 3 contiguous methylene interrupted carbon-carbon double bonds. In another aspect, greater than 40

percent of the total side chains contained within the ***thiol*** ester molecules contain sulfur.

SUMM In addition to the ***thiol*** ester composition, a process for producing the ***thiol*** ester composition is advantageously provided as another embodiment of the present invention. To produce the ***thiol*** ester composition, hydrogen sulfide is contacted with an unsaturated ester composition. The unsaturated ester composition includes unsaturated esters that have an average of at least 1.5 ester groups per unsaturated ester molecule. The unsaturated esters also have an average of at least 1.5 carbon-carbon double bonds per unsaturated ester molecule. The hydrogen sulfide and the unsaturated esters are reacted to produce or form the ***thiol*** ester composition. The ***thiol*** ester composition advantageously includes ***thiol*** ester molecules that have a molar ratio of cyclic sulfides to ***thiol*** groups of less than 1.5.

SUMM Another process for producing the ***thiol*** ester composition is advantageously provided as another embodiment of the present invention. In this process embodiment, the hydrogen sulfide and the unsaturated ester composition are contacted. The unsaturated ester composition includes unsaturated esters having an average of at least 1.5 ester groups per unsaturated ester molecule and having an average of at least 1.5 carbon-carbon double bonds per unsaturated ester molecule. The hydrogen sulfide and the unsaturated esters are then reacted in a substantial absence of a solvent to form the ***thiol*** ester composition. The ***thiol*** ester composition includes ***thiol*** ester molecules. The ***thiol*** ester composition advantageously includes ***thiol*** ester molecules that have a molar ratio of cyclic sulfides to ***thiol*** groups of less than 1.5.

SUMM The resulting ***thiol*** ester molecules produced by this process possess advantageous characteristics. For example, in some embodiments, the ***thiol*** ester molecules have a molar ratio of the hydrogen

sulfide to carbon-carbon double bonds of greater than 2. As another example, in other embodiments, the ***thiol*** ester molecules have an average of greater than 5 weight percent ***thiol*** sulfur. In some aspects, greater than 40 percent of the ***thiol*** ester molecule total side chains contain sulfur.

SUMM As another embodiment of the present invention, another process for preparing the ***thiol*** ester composition is advantageously provided. In this embodiment, a polyol composition and a ***thiol*** carboxylic acid composition are contacted and reacted to produce the ***thiol*** ester composition. The ***thiol*** ester composition includes ***thiol*** ester molecules having an average of at least 1.5 ester groups per ***thiol*** ester molecule and having an average of at least 1.5 ***thiol*** groups per ***thiol*** ester molecule.

SUMM In addition to the ***thiol*** ester composition, other compositions are advantageously provided as embodiments of the present invention. For example, a hydroxy ***thiol*** ester composition is provided as another embodiment of the present invention. The hydroxyl ***thiol*** ester composition includes hydroxy ***thiol*** ester molecules having an average of at least 1.5 ester groups per hydroxy ***thiol*** ester molecule and having an average of at least 1.5 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule.

SUMM As described herein, the .alpha.-hydroxy ***thiol*** groups contain an alcohol or hydroxy group and a ***thiol*** group within the same group. In embodiments of the present invention, the .alpha.-hydroxy ***thiol*** groups can be replaced with separate alcohol and ***thiol*** groups. In these embodiments, the same number of .alpha.-hydroxy groups can be used for the separate alcohol and ***thiol*** groups. For example, in some embodiments, the hydroxy ***thiol*** ester molecules have an average of at least 1.5 .alpha.-hydroxy ***thiol*** groups. In embodiments that contain separate alcohol and ***thiol*** groups, the hydroxy ***thiol*** ester molecules would contain an average of at least 1.5 alcohol

groups

and an average of at least 1.5 ***thiol*** groups.

SUMM In some aspects, the hydroxy ***thiol*** ester molecules have an average ranging from 1.5 to 9 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule. In some embodiments, the ***thiol*** ester molecules have a molar ratio of carbon-carbon double bonds to ***thiol*** groups of less than 1.5.

SUMM In some embodiments, the ***thiol*** ester molecules are produced from unsaturated esters that have an average of less than 25 weight percent of side chains that include 3 contiguous methylene interrupted carbon-carbon double bonds. In another aspect, greater than 40 percent of the total side chains contained within the .alpha.-hydroxy ***thiol*** ester molecules contain sulfur.

SUMM The amount of ***thiol*** sulfur contained within the hydroxy ***thiol*** ester molecules can also vary. For example, in some embodiments, the hydroxy ***thiol*** ester molecules have an average of greater than 5 weight percent ***thiol*** sulfur. In other embodiments, the hydroxy ***thiol*** ester molecules have an average ranging from 8 to 10 weight percent ***thiol*** sulfur.

SUMM In some embodiments, the hydroxy ***thiol*** ester molecules have a molar ratio of ***epoxide*** groups to the .alpha.-hydroxy ***thiol*** groups of less than 2. In other aspects, the composition is substantially free of ***epoxide*** groups.

SUMM In addition to the hydroxy ***thiol*** ester composition, methods or processes for making the hydroxy ***thiol*** ester composition are advantageously provided as embodiments of the present invention. In an embodiment, a process for preparing the hydroxy ***thiol*** ester composition is provided that includes the step of contacting the hydrogen sulfide and an epoxidized unsaturated ester composition. The epoxidized unsaturated ester composition includes epoxidized unsaturated esters having an average of at least 1.5 ester groups per epoxidized unsaturated ester molecule and having an average of at least 1.5 ***epoxide*** groups per epoxidized unsaturated ester molecule. The hydrogen sulfide and the epoxidized unsaturated esters are then

reacted

to form the hydroxy ***thiol*** ester composition.

SUMM In some embodiments, a molar ratio of the hydrogen sulfide to ***epoxide*** groups in the epoxidized unsaturated esters is greater than 1.

SUMM Another process for preparing the hydroxy ***thiol*** ester composition is advantageously provided as another embodiment of the present invention. In this process embodiment, a polyol composition and a hydroxy ***thiol*** carboxylic acid composition are contacted and reacted to produce the hydroxy ***thiol*** ester composition. In this embodiment, the hydroxy ***thiol*** ester composition includes hydroxy ***thiol*** ester molecules having an average of at least 1.5 ester groups per hydroxy ***thiol*** ester molecule and having an average of at least 1.5 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule.

SUMM A cross-linked ***thiol*** ester composition is advantageously provided as another embodiment of the present invention. The cross-linked ***thiol*** ester composition includes ***thiol*** ester oligomers having at least two ***thiol*** ester monomers connected by a polysulfide linkage having a structure --S.sub.Q--, wherein Q is greater than 1. In some embodiments, the ***thiol*** ester oligomers have at least three ***thiol*** ester monomers connected by polysulfide linkages. In another aspect, the ***thiol*** ester oligomers have from 3 to 20 ***thiol*** ester monomers connected by polysulfide linkages.

SUMM In an aspect, the cross-linked ***thiol*** ester composition includes both ***thiol*** ester monomers and ***thiol*** ester oligomers. In some embodiments, the ***thiol*** ester monomers and ***thiol*** ester oligomers have a total ***thiol*** sulfur content ranging from 0.5 to 8 weight percent; or alternatively, ranging from 8 to 15 weight percent. The combined ***thiol*** ester monomers and ***thiol*** ester oligomers can have an average molecular weight greater than 2000; or alternatively, in a range from 2000 to 20,000.

SUMM As another embodiment of the present invention, a cross-linked ***thiol*** ester composition produced by the process comprising the steps of contacting the ***thiol*** ester composition with an oxidizing agent and reacting the ***thiol*** ester and the oxidizing agent to form ***thiol*** ester oligomers is advantageously provided. In this embodiment, the ***thiol*** ester oligomers have at least two ***thiol*** ester monomers connected by a polysulfide linkage having a structure --S.sub.Q--, wherein Q is greater than 1.

SUMM A process to produce the cross-linked ***thiol*** ester composition is also advantageously provided as another embodiment of the present invention. In this process, a ***thiol*** ester composition is contacted and reacted with an oxidizing agent to form ***thiol*** ester oligomers having at least two ***thiol*** ester monomers connected by a polysulfide linkage having a structure --S.sub.Q--, wherein Q is greater than 1. In some embodiments, the oxidizing agent is elemental sulfur, oxygen, or hydrogen peroxide. In an aspect, the oxidizing agent is elemental sulfur.

SUMM In an aspect, the ***thiol*** ester is a hydroxy ***thiol*** ester. In other aspects, a weight ratio of elemental sulfur to ***thiol*** sulfur in the ***thiol*** ester molecules ranges from 0.5 to 32.

SUMM The step of the reacting the ***thiol*** ester and the oxidizing agent can be performed at a temperature ranging from 25.degree. C. to 150.degree. C. The process for producing the cross-linked ***thiol*** ester composition can also include the step of stripping residual hydrogen sulfide from the cross-linked ***thiol*** ester composition produced. In another aspect, the reaction of the ***thiol*** ester and the elemental sulfur is catalyzed. In some embodiments, the catalyst is an amine.

SUMM In another of its aspects, the present invention relates to a controlled release fertilizer material comprising a particulate plant nutrient surrounded by a coating which is the reaction product of a mixture comprising: (i) a first component selected from an

isocyanate and/or an epoxy resin, and (ii) a first active hydrogen-containing compound selected from the group consisting of a ***thiol*** ester composition; a hydroxy ***thiol*** ester composition; a cross-linked ***thiol*** ester composition and mixtures thereof.

SUMM In another of its aspects, the present invention relates to a process for the production of abrasion resistant polythiourethane and/or epoxy polymer encapsulated controlled release fertilizer particles by incorporating in urethane and/or epoxy polymer forming reaction mixture a sulfur-containing compound such as one or more of a ***thiol*** ester composition; a hydroxy ***thiol*** ester composition; a cross-linked ***thiol*** ester composition, other sulfur-based compounds described herein below and mixtures thereof.

SUMM Preferably, for the production of the present polythiourethane encapsulated controlled release fertilizer material, a sulfur-containing compound (e.g., one or more of a ***thiol*** ester composition; a hydroxy ***thiol*** ester composition; a cross-linked ***thiol*** ester composition) is used as one of the isocyanate-reactive components (alone or in combination with other active hydrogen-containing compounds). Preferably, the sulfur-containing compound comprises a sulfur-containing vegetable oil. In one preferred embodiment, the sulfur-containing vegetable oil comprises a mercaptanized vegetable oil (MVO), more preferably as described in more detail herein, even more preferably an MVO produced by the addition of hydrogen sulfide to a vegetable oil. In another preferred embodiment, the sulfur-containing vegetable oil comprises mercapto-hydroxy vegetable oil (MHVO), more preferably as described in more detail herein, even more preferably an MHVO produced by the addition of hydrogen sulfide to epoxidized vegetable oil. In yet another preferred embodiment, the sulfur-containing vegetable oil comprises sulfur cross-linked mercaptanized vegetable oil (CMVO), more preferably as described in more detail herein, even more preferably an CMVO produced by the addition of elemental sulfur to mercaptanized vegetable oil (MVO).

SUMM Preferably, for the production of epoxy polymer encapsulated controlled release fertilizer material, a sulfur-containing compound (e.g., one or

more of a ***thiol*** ester composition; a hydroxy ***thiol*** ester composition; a cross-linked ***thiol*** ester composition) is used as one of the isocyanate-reactive components (alone or in combination with other active hydrogen-containing compounds). Preferably, the sulfur-containing compound comprises a sulfur-containing vegetable oil (e.g., MVO and/or MHVO and/or CMVO) is used as one of the epoxy resin-reactive components.

DRWD FIG. 1 includes two graphs that compare the NMR's of soybean oil, which is shown in the top graph, and a ***thiol*** containing ester produced from soybean oil in accordance with an embodiment of the present invention, which is shown in the bottom graph; DRWD FIG. 2 includes two graphs that compare the NMR's of epoxidized soybean oil, which is shown in the top graph, and a ***thiol*** containing ester produced from epoxidized soybean oil in accordance with an embodiment of the present invention, which is shown in the bottom graph; DRWD FIG. 3 is a gas chromatograph (GC)/mass spectrometer (MS) trace of a ***thiol*** containing ester that was produced from soybean oil in accordance with an embodiment of the present invention and then treated by methanolysis;

DRWD FIG. 5 is a GC/MS trace of hydroxy ***thiol*** containing ester produced from epoxidized soybean oil in accordance with an embodiment of the present invention and then treated by methanolysis; DEDT In this specification, " ***thiol*** ester composition" refers to an ester composition that includes " ***thiol*** ester molecules." The ***thiol*** ester molecule has at least one ***thiol*** group and at least one ester group within the ***thiol*** ester molecule. DEDT In this specification, "hydroxy ***thiol*** ester composition" refers to an ester composition that includes "hydroxy ***thiol*** ester molecules." The hydroxy ***thiol*** ester molecule has at least one ***thiol*** group, at least one ester group, and at least one hydroxy or alcohol group within the hydroxy ***thiol*** ester molecule. Alternatively, the alcohol group and the ***thiol*** group can be combined in the same group, which is referred to as an ".alpha.-hydroxy ***thiol*** group." DEDT In this specification, "polythiourethane" refers to a urethane composition that includes more than one of the following

structure:

##STR1## The presence of the thiourethane group can be determined by method known to those skilled in the art (for example infrared spectroscopy, Raman spectroscopy, and/or NMR). ***Thiol***

Ester Composition

DETD The present invention advantageously provides a ***thiol*** ester composition as an embodiment of the present invention. The ***thiol*** ester composition includes ***thiol*** ester molecules that have an average of at least 1.5 ester groups and an average of at least 1.5 ***thiol*** groups per ***thiol*** ester molecule. The ***thiol*** ester composition also has a molar ratio of cyclic sulfides to ***thiol*** groups of less than 1.5, as described herein.

DETD Generally, the ***thiol*** ester composition contains molecules having at least one ester group and at least one ***thiol*** group. The ***thiol*** ester composition of this invention can be produced from any unsaturated ester, as described herein. Because the feedstock unsaturated esters can contain multiple carbon-carbon double bonds per unsaturated ester molecule, carbon-carbon double bond reactivity and statistical probability dictate that each ***thiol*** ester molecule of the ***thiol*** ester composition produced from the unsaturated ester composition will not have the same number of ***thiol*** groups, number of unreacted carbon-carbon double bonds, number of cyclic sulfides, molar ratio of carbon-carbon double bonds to ***thiol*** groups, molar ratio of cyclic sulfides to ***thiol*** groups and other quantities of functional groups and molar ratios disclosed herein as the feedstock unsaturated ester. Additionally, the feedstock unsaturated esters can also comprise a mixture of individual unsaturated esters having a different number of carbon-carbon double bonds and/or ester groups. Thus, many of these properties will be discussed as an average number of the groups per ***thiol*** ester molecule within the ***thiol*** ester composition or average ratio per ***thiol*** ester molecule within the ***thiol*** ester composition. In other embodiments, it is desired to control the content of ***thiol***

sulfur present in the ***thiol*** ester. Because it is difficult to ensure that the hydrogen sulfide reacts with every carbon-carbon double bond within the unsaturated ester, certain molecules of ***thiol*** ester can have more or less ***thiol*** groups than other molecules.

Thus, the weight percent of ***thiol*** groups is stated as an average across all ***thiol*** ester molecules of the ***thiol*** ester composition.

DETD The ***thiol*** ester can be derived from any unsaturated ester described herein.

DETD The ***thiol*** ester compositions can be described as comprising one or more separate or discreet functional groups of the ***thiol*** ester molecule and/or ***thiol*** ester composition. These independent functional groups can include: the number of (or average

number of) ester groups per ***thiol*** ester molecule, ***thiol*** containing the number of (or average number of) ***thiol*** groups per ***thiol*** ester molecule, the number of

(or average number of) unreacted carbon-carbon double bonds per ***thiol*** ester molecule, the average ***thiol*** sulfur content

of the ***thiol*** ester composition, the percentage (or average

percentage) of sulfide linkages per ***thiol*** ester molecule, and the percentage (or average percentage) of cyclic sulfide groups

per ***thiol*** ester molecule. Additionally, the ***thiol*** ester compositions can be described using individual or a combination of

ratios including the ratio of double bonds to ***thiol*** groups, the ratio of cyclic sulfides to ***mercaptan*** group, and the like.

As separate elements, these functional groups of the ***thiol***

composition will be described separately.

DETD Minimally, in some embodiments, the ***thiol*** ester contains

thiol ester molecules having at least one ester group and one

thiol group per ***thiol*** ester molecule. As the ***thiol*** ester is prepared from unsaturated esters, the ***thiol*** ester can contain the same number of ester groups

as the unsaturated esters described herein. In an embodiment, the ***thiol*** ester molecules have an average of at least 1.5 ester groups per ***thiol*** ester molecule. Alternatively, the ***thiol*** ester

molecules have an average of at least 2 ester groups per ***thiol*** ester molecule; alternatively, an average of at least 2.5 ester groups per ***thiol*** ester molecule; or alternatively, an average of at least 3 ester groups per ***thiol*** ester molecule. In other embodiments, the ***thiol*** esters have an average of from 1.5 to 8 ester groups per ***thiol*** ester molecule; alternatively, an average of from 2 to 7 ester groups per ***thiol*** ester molecule; alternatively, an average of from 2.5 to 5 ester groups per ***thiol*** ester molecule; or alternatively, an average of from 3 to 4 ester groups per ***thiol*** ester molecule. In yet other embodiments, the ***thiol*** ester comprises an average of 3 ester groups per ***thiol*** ester molecule or alternatively, an average of 4 ester groups per unsaturated ester molecule.

DETD Minimally, the ***thiol*** ester comprises an average of at least one ***thiol*** group per ***thiol*** ester molecule. In an embodiment, the ***thiol*** ester molecules have an average of at least 1.5 ***thiol*** groups per ***thiol*** ester molecule; alternatively, ***thiol*** containing an average of at least 2 ***thiol*** groups per ***thiol*** ester molecule; alternatively, an average of at least 2.5 ***thiol*** groups per ***thiol*** ester molecule; or alternatively, an average of at least 3 ***thiol*** groups per ***thiol*** ester molecule. In other embodiments, the ***thiol*** ester molecules have an average of from 1.5 to 9 ***thiol*** groups per ***thiol*** ester molecule; alternatively, an average of from 3 to 8 ***thiol*** groups per ***thiol*** ester molecule; alternatively, ***thiol*** containing an average of from 2 to 4 ***thiol*** groups per ***thiol*** ester molecule, or alternatively, an average of from 4 to 8 ***thiol*** groups per ***thiol*** ester molecule.

DETD In other embodiments, the ***thiol*** ester can be described by the average amount of ***thiol*** sulfur present in ***thiol*** ester. In an embodiment, the ***thiol*** ester molecules have an average of at least 5 weight percent ***thiol*** sulfur per ***thiol*** ester molecule; alternatively, an average of at least 10

weight percent ***thiol*** sulfur per ***thiol*** ester molecule, or alternatively, an average of greater than 15 weight percent ***thiol*** sulfur per ***thiol*** ester molecule. In an embodiment, the ***thiol*** ester molecules have an average of from 5 to 25 weight percent ***thiol*** sulfur per ***thiol*** ester molecule; alternatively, an average of from 5 to 20 weight percent ***thiol*** sulfur per ***thiol*** ester molecule; alternatively, an average of from 6 to 15 weight percent ***thiol*** sulfur per ***thiol*** ester molecule; or alternatively, an average of from 8 to 10 weight percent ***thiol*** sulfur per ***thiol*** ester molecule.

DETD Generally, the location of the ***thiol*** group of the ***thiol*** ester is not particularly important and will be dictated by the method used to produce the ***thiol*** ester. In embodiments wherein the ***thiol*** ester is produced by contacting an unsaturated ester, the position of the ***thiol*** group will be dictated by the position of the carbon-carbon double bond. When the carbon-carbon double bond is an internal carbon-carbon double bond, the method of producing the ***thiol*** ester will result in a secondary ***thiol*** group. However, when the double bond is located at a terminal position it is possible to choose reaction conditions to produce a ***thiol*** ester comprising either a primary ***thiol*** group or a secondary ***thiol*** group.

DETD Some methods of producing the ***thiol*** ester composition can additionally create sulfur containing functional groups other than a ***thiol*** group. For example, in some ***thiol*** ester production methods, an introduced ***thiol*** group can react with a carbon-carbon double bond within the same unsaturated ester to produce a sulfide linkage. When the reaction is with a double bond of a second unsaturated ester, this produces a simple sulfide linkage. However, in some instances, the second carbon-carbon double bond is located in the same unsaturated ester molecule. When the ***thiol*** group reacts with a second carbon-carbon double bond within the same unsaturated ester molecule, a sulfide linkage is produced. In some instances, the carbon-carbon double bond can be within a second ester group of

the unsaturated ester molecule. While in other instances, the carbon-carbon double bond can be within the same ester group of the unsaturated ester molecule.

DETD When the ***thiol*** group reacts with the carbon-carbon double bond in a second ester group of the same unsaturated ester molecule, the cyclic sulfide would contain two ester groups contained within a ring structure. When the ***thiol*** group reacts with the carbon-carbon double bond within the same ester group, the cyclic sulfide would not contain an ester group within the ring structure. Within this specification, this second type of cyclic sulfide is referred to as a cyclic sulfide. Within this specification, the first type of cyclic sulfide is referred to as a simple sulfide. In the cyclic sulfide case, the sulfide linkage produces a cyclic sulfide functionality within a single ester group of the ***thiol*** ester. This linkage is termed a cyclic sulfide for purposes of this application. One such sulfide group that can be produced is a cyclic sulfide. The cyclic sulfide rings that can be produced include a tetrahydrothiopyran ring, a thietane ring, or a thiophane ring (tetrahydrothiophene ring).

DETD In some embodiments, it is desirable to control the average amount of sulfur present as cyclic sulfide in the ***thiol*** ester. In an embodiment the average amount of sulfur present as cyclic sulfide in the ***thiol*** ester molecules comprises less than 30 mole percent.

Alternatively, the average amount of sulfur present as cyclic sulfide in the ***thiol*** esters comprises less than 20 mole percent; alternatively, less than 10 mole percent; alternatively, less than 5 mole percent; or alternatively, less than 2 mole percent. In other embodiments, it is desired to control the molar ratio of cyclic sulfides to ***thiol*** groups. In other embodiments, it is desirable to have molar ratios of cyclic sulfide to ***thiol*** group. In an embodiment, the average molar ratio of cyclic sulfide groups to ***thiol*** group per ***thiol*** ester is less than 1.5. Alternatively, the average molar ratio of cyclic sulfide groups to ***thiol*** group per ***thiol*** ester is less than 1; alternatively, less than 0.5; alternatively, less than 0.25; or

alternatively, 0.1. In some embodiments, the ratio of cyclic sulfide groups to ***thiol*** group per ***thiol*** ester ranges from 0 to 1; or alternatively, the average molar ratio of cyclic sulfide groups to ***thiol*** group per ***thiol*** ester ranges between 0.05 and 1.

DETD In some instances it can desirable to have carbon-carbon double bonds present in the ***thiol*** ester composition while in other embodiments it can be desirable to minimize the number of carbon-carbon double bonds present in the ***thiol*** ester composition.

The presence of carbon-carbon double bonds present in the ***thiol*** ester can be stated as an average molar ratio of carbon-carbon double bonds to ***thiol*** -sulfur. In an embodiment, the average ratio of the remaining unreacted carbon-carbon double bond in the ***thiol*** ester composition to ***thiol*** sulfur is less than 1.5 per ***thiol*** ester molecule. Alternatively, the average ratio of carbon-carbon double bond to ***thiol*** sulfur is less than 1.2 per 1.2 per ***thiol*** ester molecule; alternatively, less than 1.0 per ***thiol*** ester molecule; alternatively, less than 0.75 per ***thiol*** ester molecule; alternatively, less than 0.5 per ***thiol*** ester molecule; alternatively, less than 0.2 per ***thiol*** ester molecule; or alternatively, less than 0.1 per ***thiol*** ester molecule.

DETD In particular embodiments, the ***thiol*** ester is produced from unsaturated ester compositions. Because the feedstock unsaturated ester has particular compositions having a certain number of ester groups present, the product ***thiol*** ester composition will have about the same number of ester groups per ***thiol*** ester molecule as the feedstock unsaturated ester. Other, independent ***thiol*** ester properties described herein can be used to further describe the ***thiol*** ester composition.

DETD In some embodiments, the ***thiol*** ester molecules are produced from unsaturated esters having an average of less than 25 weight percent of side chains having 3 contiguous methylene interrupted carbon-carbon double bonds, as described herein. In some embodiments, greater than 40 percent of the ***thiol*** containing natural source total side

chains can include sulfur. In some embodiments, greater than 60 percent of the ***thiol*** ester molecule total side chains can include sulfur. In other embodiments, greater than 50, 70, or 80 percent of the ***thiol*** ester molecule total side chains can include sulfur.

DETD In an embodiment, the ***thiol*** ester is a ***thiol*** containing natural source oil, as described herein. When the ***thiol*** ester is a ***thiol*** containing natural source oil, functional groups that are present in the ***thiol*** containing natural source oil can be described in a "per ***thiol*** ester molecule" basis or in a "per triglyceride" basis. The ***thiol*** containing natural source oil can have substantially the same properties as the ***thiol*** ester composition, such as the molar ratios and other independent descriptive elements described herein.

DETD The average number of ***thiol*** groups per triglyceride in the ***thiol*** containing natural source oil is greater than about 1.5.

In some embodiments, the average number of ***thiol*** groups per triglyceride can range from about 1.5 to about 9.

DETD The ***thiol*** ester compositions can also be described as a product produced by the process comprising contacting hydrogen sulfide and an unsaturated ester composition and can be further limited by the process as described herein. The ***thiol*** containing natural source oil can also be described using a molecular weight or an average molecular weight of the side chains.

DETD Hydroxy ***Thiol*** Ester Composition

DETD In embodiments of the present invention, the ***thiol*** ester compositions can also contain a hydroxy or alcohol group. When the ***thiol*** ester composition includes the hydroxy group, the ***thiol*** ester composition is referred to herein as the hydroxy ***thiol*** ester composition. The quantity or number of alcohol groups present in the hydroxy ***thiol*** ester composition can be independent of the quantity of other functional groups present in the hydroxy ***thiol*** ester composition (i.e. ***thiol*** groups, ester groups, sulfides, cyclic sulfides). Additionally, the weight percent of ***thiol*** sulfur and functional group ratios

(i.e. molar ratio of cyclic sulfides to ***thiol*** groups, molar ratio of ***epoxide*** groups to ***thiol*** groups, molar ratio of ***epoxide*** groups to .alpha.-hydroxy ***thiol*** groups and other disclosed quantities of functional groups and their molar ratios to the ***thiol*** groups) are separate or discreet elements that can be used to describe the hydroxy ***thiol*** ester composition. The hydroxy ***thiol*** ester composition can be described using any combination of the hydroxy ***thiol*** ester composition separate functional groups or ratios described herein.

DETD In an embodiment, the hydroxy ***thiol*** ester composition is produced by reacting hydrogen sulfide with an epoxidized unsaturated ester composition as described herein. Because the epoxidized unsaturated ester can contain multiple ***epoxide*** groups, ***epoxide*** group reactivity and statistical probability dictate that not all hydroxy ***thiol*** ester molecules of the hydroxy ***thiol*** ester composition will have the same number of hydroxy groups, ***thiol*** groups, .alpha.-hydroxy ***thiol*** groups, sulfides, cyclic sulfides, molar ratio of cyclic sulfides to ***thiol*** groups, molar ratio of ***epoxide*** groups to ***thiol*** groups, molar ratio of ***epoxide*** groups to .alpha.-hydroxy ***thiol*** groups, weight percent ***thiol*** sulfur and other disclosed quantities of functional groups and their molar ratios as the epoxidized unsaturated ester composition. Thus, many of these properties will be discussed as an average number or ratio per hydroxy ***thiol*** ester molecule. In other embodiments, it is desired to control the content of ***thiol*** sulfur present in the hydroxy ***thiol*** ester. Because it is difficult to ensure that the hydrogen sulfide reacts with every ***epoxide*** group within the epoxidized unsaturated ester, certain hydroxy ***thiol*** ester molecules can have more or less ***thiol*** groups than other molecules within the hydroxy ***thiol*** ester composition. Thus, the weight percent of ***thiol*** groups can be stated as an average

weight percent across all hydroxy ***thiol*** ester molecules.

DETD As an embodiment of the present invention, the hydroxy ***thiol*** ester composition includes hydroxy ***thiol*** ester molecules that have an average of at least 1 ester groups and an average of at least 1 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule. As an embodiment of the present invention, the hydroxy ***thiol*** ester composition includes hydroxy ***thiol*** ester molecules that have an average of at least 1.5 ester groups and an average of at least 1.5 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule.

DETD Minimally, in some embodiments, the hydroxy ***thiol*** ester comprises at least one ester, at least one ***thiol*** group, and at least one hydroxy group. Because the hydroxy ***thiol*** ester is prepared from epoxidized unsaturated esters, the hydroxy ***thiol*** ester can contain the same number of ester groups as the epoxidized unsaturated esters. In an embodiment, the hydroxy ***thiol*** ester molecules have an average of at least 1.5 ester groups per hydroxy ***thiol*** ester molecule. Alternatively, the hydroxy ***thiol*** ester molecules have an average of at least 2 ester groups per hydroxy ***thiol*** ester molecule; alternatively, an average of at least 2.5 ester groups per hydroxy ***thiol*** ester molecule; or alternatively, an average of at least 3 ester groups per hydroxy ***thiol*** ester molecule. In other embodiments, the hydroxy ***thiol*** esters have an average of from 1.5 to 8 ester groups per hydroxy ***thiol*** ester molecule; alternatively, an average of from 2 to 7 ester groups per hydroxy ***thiol*** ester molecule; alternatively, an average of from 2.5 to 5 ester groups per hydroxy ***thiol*** ester molecule; or alternatively, an average of from 3 to 4 ester groups per hydroxy ***thiol*** ester molecule. In yet other embodiments, the .alpha.-hydroxy ***thiol*** ester comprises an average of 3 ester groups per hydroxy ***thiol*** ester molecule or alternatively, an average of 4 ester groups per hydroxy ***thiol*** ester molecule.

DETD In some embodiments, the hydroxy group and the ***thiol*** group are combined in the same group, which produces the .alpha.-hydroxy ***thiol*** group. In other embodiments, the ***thiol*** group and the hydroxy or alcohol group are not in the same group. When this occurs, to produce the hydroxy ***thiol*** ester composition, the hydroxy group is added independently of the ***thiol*** group. For example, as another embodiment of the present invention, the hydroxy ***thiol*** ester composition advantageously includes hydroxy ***thiol*** ester molecules. The hydroxy ***thiol*** ester molecules have an average of at least 1.5 ester groups, an average of at least 1.5 ***thiol*** groups, and an average of at least 1.5 alcohol groups per hydroxy ***thiol*** ester molecule.

DETD Minimally, in some embodiments, the hydroxy ***thiol*** ester comprises at least one ***thiol*** group per hydroxy ***thiol*** ester molecule. In an embodiment, the hydroxy ***thiol*** ester molecules have an average of at least 1.5 ***thiol*** groups per hydroxy ***thiol*** ester molecule; alternatively, an average of at least 2 ***thiol*** groups per hydroxy ***thiol*** ester molecule; alternatively, an average of at least 2.5 ***thiol*** groups per hydroxy ***thiol*** ester molecule; or alternatively, an average of at least 3 ***thiol*** groups per hydroxy ***thiol*** ester molecule. In other embodiments, the hydroxy ***thiol*** ester molecules have an average of from 1.5 to 9 ***thiol*** groups per hydroxy ***thiol*** ester molecule; alternatively, an average of from 3 to 8 ***thiol*** groups per hydroxy ***thiol*** ester molecule; alternatively, an average of from 2 to 4 ***thiol*** groups per hydroxy ***thiol*** ester molecule; or alternatively, an average of from 4 to 8 ***thiol*** groups per hydroxy ***thiol*** ester.

DETD Minimally, in some embodiments, the hydroxy ***thiol*** ester composition comprises an average of at least 1 hydroxy or alcohol group per hydroxy ***thiol*** ester molecule. In some embodiments, the hydroxy ***thiol*** ester composition comprises an average of at least 1.5 hydroxy groups per hydroxy ***thiol*** ester.

molecule;
alternatively, average of at least 2 hydroxy groups per hydroxy
thiol ester molecule; alternatively, an average of at
least 2.5
hydroxy groups per hydroxy ***thiol*** ester molecule; or
alternatively, an average of at least 3 hydroxy groups per
thiol
ester molecule. In other embodiments, the ***thiol*** ester
composition comprises an average of from 1.5 to 9 hydroxy groups
per
hydroxy ***thiol*** ester molecule; alternatively, an average
of
from 3 to 8 hydroxy groups per hydroxy ***thiol*** ester
molecule;
alternatively, an average of from 2 to 4 hydroxy groups per
hydroxy ***thiol*** ester molecule; or alternatively, an average of
from 4 to
8 hydroxy groups per hydroxy ***thiol*** ester molecule.
DETD In yet other embodiments, the number of hydroxy groups can be
stated as
an average molar ratio of hydroxy group to ***thiol***
groups.
Minimally, in some embodiments, the molar ratio of hydroxy groups
to
thiol groups is at least 0.25. In some embodiments, the
molar ratio of hydroxy groups to ***thiol*** groups is at least
0.5;
alternatively, at least 0.75; alternatively, at least 1.0;
alternatively, at least 1.25; or alternatively, at least 1.5. In
other
embodiments, the molar ratio of hydroxy groups to ***thiol***
groups
ranges from 0.25 to 2.0; alternatively, from 0.5 to 1.5; or
alternatively, from 0.75 to 1.25.
DETD In embodiments where the hydroxy ***thiol*** esters are
produced
from an epoxidized unsaturated ester, the hydroxy ***thiol***
esters
can be described as containing ester groups and .alpha.-hydroxy
thiol groups. The number of ester groups and the number
of
.alpha.-hydroxy ***thiol*** groups are independent elements
and as
such the hydroxy ***thiol*** esters can be described as
having any
combination of ester groups and .alpha.-hydroxy ***thiol***
groups
described herein. Minimally, the hydroxy ***thiol*** ester
comprises
an average of at least 1 .alpha.-hydroxy ***thiol*** group
per
hydroxy ***thiol*** ester molecule. In some embodiments, the
hydroxy ***thiol*** ester composition comprises an average of at
least 1.5
.alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol***
ester
molecule; alternatively, an average of at least 2 .alpha.-hydroxy

thiol groups per hydroxy ***thiol*** ester molecule; alternatively, an average of at least 2.5 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule; or alternatively, an average of at least 3 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule. In other embodiments, the hydroxy ***thiol*** ester composition comprises an average of from 1.5 to 9 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule; alternatively, an average of from 3 to 8 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule; alternatively, an average of from 2 to 4 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule; or alternatively, an average of from 4 to 8 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule.

DETD The hydroxy ***thiol*** esters can be produced by contacting an epoxidized ester derived from an unsaturated ester (i.e., epoxidized unsaturated ester), as described herein. In some instances it can be desirable to have ***epoxide*** groups present in the hydroxy ***thiol*** ester composition. While in other embodiments, it can be desirable to minimize the number of epoxy groups present in the hydroxy ***thiol*** ester composition. Thus, the presence of residual ***epoxide*** groups can be another separate functional group used to describe the hydroxy ***thiol*** ester.

DETD The presence of ***epoxide*** groups in the hydroxy ***thiol*** ester can be independently described as an average number of ***epoxide*** groups per hydroxy ***thiol*** ester, a molar ratio of ***epoxide*** groups to ***thiol*** groups, a molar ratio of ***epoxide*** groups to .alpha.-hydroxy ***thiol*** groups, or any combination thereof. In some embodiments, the hydroxy ***thiol*** ester molecules comprise an average of less than 2 ***epoxide*** groups per hydroxy ***thiol*** ester molecule, i.e., the hydroxy ***thiol*** ester molecules have a molar ratio of ***epoxide*** groups to .alpha.-hydroxy ***thiol*** groups of less than 2. Alternatively, the hydroxy ***thiol*** ester comprises an average of less than 1.5 ***epoxide*** groups per hydroxy ***thiol*** ester molecule; alternatively, an average of less than 1

epoxide group per hydroxy ***thiol*** ester molecule; alternatively, an average of less than 0.75 ***epoxide*** groups per hydroxy ***thiol*** ester molecule; or alternatively, an average of less than 0.5 ***epoxide*** groups per hydroxy ***thiol*** ester molecule. In other embodiments, the molar ratio of ***epoxide*** groups to ***thiol*** groups averages less than 1.5. Alternatively, the molar ratio of ***epoxide*** groups to ***thiol*** groups averages less than 1; alternatively, averages less than 0.75; alternatively, averages less than 0.5; alternatively, averages less than 0.25; or alternatively, averages less than 0.1. In yet other embodiments, the molar ratio of ***epoxide*** groups to .alpha.-hydroxy ***thiol*** groups averages less than 1.5. Alternatively, the molar ratio of ***epoxide*** groups to .alpha.-hydroxy ***thiol*** groups averages less than 1; alternatively, averages less than 0.75; alternatively, averages less than 0.5; alternatively, averages less than 0.25; or alternatively, averages less than 0.1.

DETD In some embodiments, the hydroxy ***thiol*** ester composition is substantially free of ***epoxide*** groups.

DETD In other embodiments, the hydroxy ***thiol*** ester can be described by the average amount of ***thiol*** sulfur present in hydroxy ***thiol*** ester. In an embodiment, the hydroxy ***thiol*** ester molecules have an average of at least 2.5 weight percent ***thiol*** sulfur per hydroxy ***thiol*** ester molecule; alternatively, an average of at least 5 weight percent ***thiol*** sulfur per hydroxy ***thiol*** ester molecule; alternatively, an average of at least 10 weight percent ***thiol*** sulfur per hydroxy ***thiol*** ester molecule; or alternatively, an average of greater than 15 weight percent ***thiol*** sulfur per hydroxy ***thiol*** ester molecule. In an embodiment, the hydroxy ***thiol*** ester molecules have an average of from 5 to 25 weight percent ***thiol*** sulfur per hydroxy ***thiol*** ester molecule; alternatively, an average of from 5 to 20 weight percent ***thiol*** sulfur per hydroxy ***thiol*** ester molecule; alternatively, an average of from 6 to 15 weight percent ***thiol*** sulfur per hydroxy ***thiol*** ester molecule; or

alternatively, an average of from 8 to 10 weight percent ***thiol*** sulfur per hydroxy ***thiol*** ester molecule.

DETD In some embodiments, at least 20 percent of the total side chains include the .alpha.-hydroxy ***thiol*** group. In some embodiments, at least 20 percent of the total side chains include the .alpha.-hydroxy ***thiol*** group. In some embodiments, at least 60 percent of the total side chains include the .alpha.-hydroxy ***thiol*** group; alternatively, at least 70 percent of the total side chains include the .alpha.-hydroxy ***thiol*** group. Yet in other embodiments, at least 80 percent of the total side chains include the .alpha.-hydroxy ***thiol*** group.

DETD In some aspects, greater than 20 percent of the hydroxy ***thiol*** ester molecule total side chains contain sulfur. In some aspects, greater than 40 percent of the hydroxy ***thiol*** ester molecule total side chains contain sulfur. In some aspects, greater than 60 percent of the hydroxy ***thiol*** ester molecule total side chains contain sulfur; alternatively, greater than 70 percent of the total side chains contain sulfur; or alternatively, greater than 80 percent of the total side chains contain sulfur.

DETD In particular embodiments, the epoxidized unsaturated ester used in the synthesis of the hydroxy ***thiol*** ester is produced from the epoxidized unsaturated ester composition that includes an epoxidized natural source oil. Because the natural source oils have particular compositions regarding the number of ester groups present, the hydroxy ***thiol*** ester will have about the same number of ester groups as the feedstock natural source oil. Other independent properties that are described herein can be used to further describe the hydroxy ***thiol*** ester.

DETD In other embodiments, the epoxidized unsaturated ester used to produce the hydroxy ***thiol*** ester is produced from synthetic (or semi-synthetic) unsaturated ester oils. Because the synthetic ester oils can have particular compositions regarding the number of ester groups present, the hydroxy ***thiol*** ester would have about the same number of ester groups as the synthetic ester oil. Other,

independent properties of the unsaturated ester, whether the unsaturated ester includes natural source or synthetic oils, can be used to further describe the hydroxy ***thiol*** ester composition.

DETD The hydroxy ***thiol*** ester compositions can also be described as a product produced by the process comprising contacting hydrogen sulfide and an epoxidized unsaturated ester composition and can be further limited by the process as described herein. The hydroxy ***thiol*** containing natural source oil can also be described using an average molecular weight or an average molecular weight of the side chains.

DETD Cross-Linked ***Thiol*** Ester Compositions

DETD In an aspect, the present invention relates to a cross-linked ***thiol*** ester composition. Generally, the cross-linked ***thiol*** ester molecules are oligomers of ***thiol*** esters that are connected together by polysulfide linkages --S.sub.x-- wherein x is an integer greater than 1. As the cross-linked ***thiol*** ester is described as an oligomer of ***thiol*** esters, the ***thiol*** esters can be described as the monomer from which the cross-linked ***thiol*** esters are produced.

DETD In an aspect, the cross-linked ***thiol*** ester composition comprises a ***thiol*** ester oligomer having at least two ***thiol*** ester monomers connected by a polysulfide linkage having a structure --S.sub.Q--, wherein Q is an integer greater than 1. In an aspect, the polysulfide linkage may be the polysulfide linkage --S.sub.Q--, wherein Q is 2, 3, 4, or mixtures thereof. In other embodiments, Q can be 2; alternatively, 3; or alternatively, 4.

DETD In an aspect, the cross-linked ***thiol*** ester composition comprises a ***thiol*** ester oligomer having at least 3 ***thiol*** ester monomers connected by polysulfide linkages; alternatively, 5 ***thiol*** ester monomers connected by polysulfide linkages; alternatively, 7 ***thiol*** ester monomers connected by polysulfide linkages; or alternatively, 10 ***thiol*** ester monomers connected by polysulfide linkages. In yet other embodiments, the cross-linked ***thiol*** ester composition comprises a ***thiol*** ester oligomer having from 3 to 20 ***thiol*** ester monomers connected by polysulfide linkages; alternatively, from 5 to 15 ***thiol*** ester monomers connected by polysulfide linkages; or alternatively, from 7 to 12 ***thiol*** ester monomers connected by polysulfide linkages.

DETD In an aspect, the cross-linked ***thiol*** ester composition comprises ***thiol*** ester monomers and ***thiol*** ester oligomers. In some embodiments, the cross-linked ***thiol*** ester composition has a combined ***thiol*** ester monomer and ***thiol*** ester oligomer average molecular weight greater than 2,000. In other embodiments, the cross-linked ***thiol*** ester composition has a combined ***thiol*** ester monomer and ***thiol*** ester oligomer average molecular weight greater than 5,000; or alternatively, greater than 10,000. In yet other embodiments, the cross-linked ***thiol*** ester composition has a combined ***thiol*** ester monomer and ***thiol*** ester oligomer average molecular weight ranging from 2,000 to 20,000; alternatively, from 3,000 to 15,000; or alternatively, from 7,500 to 12,500.

DETD In an aspect, the ***thiol*** ester monomers and ***thiol*** ester oligomers have a total ***thiol*** sulfur content greater than 0.5. In other embodiments, the ***thiol*** ester monomers and ***thiol*** ester oligomers have a total ***thiol*** sulfur content greater than 1; alternatively, greater than 2; alternatively, greater than 4. In yet other embodiments, the ***thiol*** ester monomers and the ***thiol*** ester oligomers have a total ***thiol*** sulfur content from 0.5 to 8; alternatively, from 4 to 8; or alternatively, 0.5 to 4.

DETD In an aspect, the ***thiol*** ester monomers and ***thiol*** ester oligomers have a total sulfur content greater than 8. In some embodiments, the ***thiol*** ester monomers and ***thiol*** ester oligomers have a total sulfur content greater than 10; alternatively, greater than 12. In yet other embodiments, the ***thiol*** ester monomers and ***thiol*** ester oligomers have a total sulfur content ranging from 8 to 15 weight percent; alternatively, from 9 to 14; or alternatively, from 10 to 13.

DETD The cross-linked ***thiol*** ester compositions can also be described as a product produced by the process comprising contacting a ***thiol*** ester with oxidizing agent and can be further limited by the process as described herein.

DETD The present invention advantageously includes sulfide-containing ester compositions as embodiments of the present invention. Generally, the sulfide-containing ester compositions can be described as containing

molecules having at least one ester group and a least one sulfide group within each molecule. The sulfide-containing esters used in the present invention can be produced by contacting either an unsaturated ester or an epoxidized unsaturated ester with a ***thiol*** containing compound as described herein.

DETD The feedstock unsaturated esters can contain multiple carbon-carbon double bonds per unsaturated ester molecule. The carbon-carbon double bond reactivity and statistical probability, however, dictate that each sulfide-containing ester molecule of the ***thiol*** - containing ester composition produced from the unsaturated ester composition will not have the same number of sulfide groups, number of unreacted carbon-carbon double bonds, molar ratio of carbon-carbon double bonds to sulfide groups, molar ratio of cyclic sulfides to ***thiol*** groups and other herein disclosed quantities of functional groups and molar ratios. Additionally, the feedstock unsaturated esters can also comprise a mixture of individual unsaturated esters having a different number of carbon-carbon double bonds and/or ester groups. Many of these properties are discussed herein as an average number of the groups per sulfide-containing ester molecule within the sulfide-containing ester composition or average ratio per ***thiol*** -containing ester molecule within the sulfide-containing ester composition.

DETD In embodiments related to the sulfide-containing ester that is produced from an epoxidized unsaturated ester, the feedstock epoxidized unsaturated esters can contain multiple ***epoxide*** groups per unsaturated ester molecule. Individual ***epoxide*** group reactivity and statistical probability dictate that each sulfide-containing ester molecule of the sulfide-containing ester composition produced from the unsaturated ester composition will not have the same number of sulfide groups, number of unreacted ***epoxide*** groups, molar ratio of ***epoxide*** groups to sulfide groups, and other herein disclosed quantities of functional groups and molar ratios. Additionally, the feedstock epoxidized unsaturated esters can also comprise a mixture of individual epoxidized unsaturated ester molecules having a different number of ***epoxide*** groups and/or ester groups. Thus, many of these properties are described as an average number of the groups per sulfide-containing ester molecules within the sulfide-containing ester composition or

average

ratio per ***thiol*** -containing ester molecule within the sulfide-containing ester composition.

DETD Minimally, in some embodiments, the sulfide-containing esters comprise

at least one ester group per sulfide-containing ester molecule.

In some

embodiments, the sulfide-containing ester has an average of at least 1.5

ester groups per sulfide-containing ester molecule.

Alternatively, the sulfide-containing ester molecules have an average of at least 2 ester

groups per sulfide-containing ester molecule; alternatively, an average of at least 2.5 ester groups per sulfide-containing ester molecule; or

alternatively, an average of at least 3 ester groups per sulfide-containing ester molecule. In other embodiments, the sulfide-containing esters have an average of from 1.5 to 9 ester groups per sulfide-containing ester molecule; alternatively, an average of from

1.5 to 8 ester groups per sulfide-containing ester molecule;

alternatively, an average of from 2 to 8 ester groups per sulfide-containing ester molecule; alternatively, an average of from 2

to 7 ester groups per sulfide-containing ester molecule;

alternatively, an average of from 2.5 to 5 ester groups per sulfide-containing ester molecule; alternatively, an average of from 2.5 to 5 ester groups per sulfide-containing ester molecule; or alternatively, an average of from

3 to 4 ester groups per sulfide-containing ester molecule. In yet other

embodiments, the hydroxy ***thiol*** -containing ester comprises an average of about 3 ester groups per sulfide-containing ester molecule;

or alternatively, an average of about 4 ester groups per sulfide-containing ester molecule.

DETD In some embodiments, R.sup.3 comprises at least one functional group.

In one aspect, the functional group is selected from the group consisting of a hydroxy group, a carboxylic acid group, a carboxylic

ester group, an amine group, a sulfide group, and a second

thiol

group. In some aspects, R.sup.3 comprises at least two functional groups. In some aspects, the functional groups are selected from the

group consisting of a hydroxy group, carboxylic acid group, a carboxylic

ester group, an amine group, a sulfide group, a second

thiol

group, and mixtures thereof.

DETD The sulfide-containing ester compositions can also be described as a

product produced by the process comprising contacting an unsaturated ester with a ***mercaptan*** and can be further limited by the process as described herein. In other embodiments, the sulfide-containing ester composition can also be described as a product produced by a process comprising contacting an epoxidized unsaturated ester with a ***mercaptan*** and can be further limited by the process as described herein.

DETD Generally, the thioacrylate ester composition can be described as comprising thioacrylate molecules having at least one ester group in addition to any acrylate or thioacrylate ester groups present in the thioacrylate molecule and at least one thioacrylate group. The ester group(s) that are in addition to any acrylate or thioacrylate ester groups present in the thioacrylate molecule are hereinafter referred to as "supplementary ester group(s)." The thioacrylate ester composition described herein can be produced by contacting an acrylate composition with a ***thiol*** -containing ester composition and/or a hydroxy ***thiol*** -containing ester composition, both of which are described herein.

DETD The feedstock ***thiol*** ester compositions and/or hydroxy ***thiol*** ester compositions can comprise a mixture of molecules that have an average quantity of ester groups, ***thiol*** groups, hydroxy groups, and other groups and molar ratios described herein. Additionally, individual ***thiol*** and hydroxy group reactivity within the ***thiol*** -containing ester compositions and/or hydroxy ***thiol*** ester compositions and statistical probability dictate that each thioacrylate ester molecule of the thioacrylate ester composition produced may not have the same number of ester groups, thioacrylate groups, acrylate groups, and other herein disclosed quantities of functional groups, moieties, and molar ratios. Thus, many of the properties of the thioacrylate ester molecules within the thioacrylate ester composition are described as using an average number of the groups per thioacrylate ester molecule within the thioacrylate ester composition or as an average ratio per thioacrylate ester molecule within the thioacrylate ester composition.

DETD The thioacrylate ester can also be described as a product produced by the process that includes contacting a ***thiol*** -containing ester composition with an acrylate composition and can be further limited by the process described herein. In other embodiments, the thioacrylate ester composition can also be described as a product produced by a process that includes contacting a hydroxy ***thiol*** - containing ester composition with an acrylate composition and can be further limited by the process described herein.

DETD The present invention advantageously provides a sulfonic acid-containing ester as an embodiment of the present invention. Generally, the sulfonic acid-containing ester of the present invention includes sulfonic acid-containing ester molecules having at least one ester group and a least one sulfonic acid group. The sulfonic acid-containing ester described herein can be produced by contacting a ***thiol*** ester with an oxidizing agent as described herein. Because the feedstock for the production of the sulfonic acid-containing ester can include multiple ***thiols*** groups, ***thiol*** group reactivity and statistical probability dictate that each sulfonic acid-containing ester molecule of the sulfonic acid-containing ester will not have the same number of sulfonic acid groups. Additionally, the feedstock ***thiol*** ester can also include a mixture of individual ***thiol*** ester molecules having different numbers of ***thiol*** groups and/or ester groups. Thus, many of the groups present in the sulfonic acid-containing ester are described herein as an average number of the groups per sulfonic acid-containing ester molecule or an average ratio per sulfonic acid-containing ester molecule within the sulfonic acid-containing ester.

DETD In some embodiments of the present invention, the sulfonic acid ester is substantially free of ***thiol*** groups.

DETD The sulfonic acid-containing ester can also be described as a product produced by the process comprising contacting a ***thiol*** ester with an oxidizing agent described herein.

DETD Process for Making a ***Thiol*** Ester Composition

DETD The present invention advantageously provides processes for producing a ***thiol*** ester composition as embodiments of the present invention.

As an embodiment, the present invention advantageously includes a process to produce a ***thiol*** ester composition by contacting hydrogen sulfide and an unsaturated ester composition containing unsaturated esters and reacting the hydrogen sulfide and unsaturated esters to form or produce the ***thiol*** ester composition.

As another embodiment of the present invention, a process to produce the ***thiol*** ester composition is advantageously provided. In this embodiment, the process includes contacting a composition comprising a polyol with a composition comprising a ***thiol*** containing carboxylic acid composition and reacting the polyol and ***thiol*** containing carboxylic acid composition to form the ***thiol*** ester composition.

DETD In some embodiments of the present invention that include producing ***thiol*** ester compositions, the unsaturated ester composition is a natural source oil. In an aspect, the unsaturated ester composition is soybean oil or alternatively castor oil. Other suitable types of unsaturated ester compositions are described herein and can be used in the processes for producing the ***thiol*** ester compositions.

DETD ***Thiol*** Esters from Unsaturated Esters
DETD As an embodiment of the present invention, the ***thiol*** esters described herein can be produced by a process comprising contacting hydrogen sulfide and an unsaturated ester composition and reacting hydrogen sulfide and the unsaturated ester composition to form the ***thiol*** ester composition. In one embodiment, the unsaturated ester composition includes unsaturated esters having an average of at least 1.5 ester groups and an average of at least 1.5 carbon-carbon double bonds per unsaturated ester molecule. In this embodiment, the ***thiol*** ester composition includes ***thiol*** ester molecules having a molar ratio of cyclic sulfides to ***thiol*** groups of less than 1.5.

DETD The processes for producing the ***thiol*** ester composition can be applied to any of the unsaturated esters described herein and used to produce any of the ***thiol*** esters described herein. The process for producing the ***thiol*** ester composition can also

include any additional process steps or process conditions described herein.

DETD The hydrogen sulfide to molar equivalents of unsaturated ester carbon-carbon double bonds molar ratio utilized in the process to produce the ***thiol*** ester composition can be any molar ratio that produces the desired ***thiol*** ester. The molar equivalents of unsaturated ester carbon-carbon double bonds is calculated by the equation: ##EQU1## In this equation, UES GMW is the average gram molecular weight of the unsaturated ester, UES Mass is the mass of the feedstock unsaturated ester, and UES C.dbd.C is the average number of double bonds per unsaturated ester molecule. In some embodiments, the ***thiol*** ester molecules have a molar ratio of the hydrogen sulfide to the unsaturated ester carbon-carbon double bonds of greater than 2.

In other embodiments, the hydrogen sulfide to unsaturated ester carbon-carbon double bonds molar ratio is greater than 5; alternatively, greater than 10; alternatively, greater than 15; or alternatively, greater than 20. In other embodiments, the hydrogen sulfide to unsaturated ester carbon-carbon double bonds molar ratio can be from 2 to 500; alternatively, from 5 to 200; alternatively, from 10 to 100; or alternatively, from 100 to 200.

DETD When a continuous reactor is used, a feed unsaturated ester weight hourly space velocity ranging from 0.1 to 5 can be used to produce the desired ***thiol*** ester. Alternatively, the feed unsaturated ester weight hourly space velocity ranges between 0.1 to 5; alternatively, from 0.1 to 2. Alternatively, the feed unsaturated ester weight hourly space velocity is 0.1; alternatively, the feed unsaturated ester weight hourly space velocity is 0.25; or alternatively, the feed unsaturated ester weight hourly space velocity is 2.

DETD The time required for the reaction of the unsaturated ester and hydrogen sulfide can be any time required to form the described ***thiol*** ester. Generally, the time required for the reaction of the unsaturated ester and hydrogen sulfide is at least 5 minutes.

In some embodiments, the time required for the reaction of the unsaturated ester and hydrogen sulfide ranges from 5 minutes to 72 hours; alternatively, from 10 minutes to 48 hours; or alternatively, from 15 minutes to 36 hours.

DETD In embodiments, the process to produce the ***thiol*** ester further comprises a step to remove excess or residual hydrogen sulfide after reacting the hydrogen sulfide and the unsaturated ester composition. In some embodiments, the ***thiol*** ester is vacuum stripped. In some embodiments, the ***thiol*** ester is vacuum stripped at a temperature ranging between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the ***thiol*** ester is sparged with an inert gas to remove hydrogen sulfide. In some embodiments, the ***thiol*** ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged ***thiol*** ester comprises less than 0.1 weight percent hydrogen sulfide. In other embodiments, the stripped or sparged ***thiol*** ester comprises less than 0.05 weight percent sulfur; alternatively, less than 0.025 weight percent hydrogen sulfide; or alternatively, less than 0.01 weight percent hydrogen sulfide.

DETD The reaction between the unsaturated ester and hydrogen sulfide can be performed at any temperature capable of forming the ***thiol*** ester. In some embodiments, the unsaturated ester and hydrogen sulfide can be reacted at a temperature greater than -20.degree. C. In other embodiments, the unsaturated ester and hydrogen sulfide can be reacted at a temperature greater than 0.degree. C.; alternatively, greater than 20.degree. C.; alternatively, greater than 50.degree. C.; alternatively, greater than 80.degree. C.; or alternatively, greater than 100.degree. C. In yet other embodiments, the unsaturated ester and hydrogen sulfide can be reacted at a temperature from -20.degree. C. to 200.degree. C.; alternatively, from 120.degree. C. to 240.degree. C.; alternatively, from 170.degree. C. to 210.degree. C.; alternatively, from 185.degree. C. to 195.degree. C.; alternatively, from 20.degree. C. to 200.degree. C.; alternatively, from 20.degree. C. to 170.degree. C.; or alternatively, from 80.degree. C. to 140.degree. C.

DETD ***Thiol*** esters having a low cyclic sulfide content can be produced using the disclosed process. In an aspect, the process

for producing the ***thiol*** ester forms or produces a ***thiol*** ester having a molar ratio of cyclic sulfide to ***thiol*** groups of less than 1.5. Additional cyclic sulfide to ***thiol*** groups molar ratios are disclosed herein.

DETD In addition to lower cyclic sulfide content, ***thiol*** esters having a low carbon-carbon double bond to ***thiol*** group molar ratio can also be produced using the disclosed process. In an aspect, the process described herein produces the ***thiol*** ester having a carbon-carbon double bond to ***thiol*** group molar ratio of less than 1.5. Additional carbon-carbon double bond to ***thiol*** group molar ratios are disclosed herein.

DETD In some aspects, the process described herein produces the ***thiol*** ester molecules having an average of greater than 5 weight percent ***thiol*** sulfur. Additional ***thiol*** sulfur contents are disclosed herein. In other aspects, the process for producing a ***thiol*** ester forms a ***thiol*** ester having greater than 40 percent of the ***thiol*** ester total side chains include sulfur. Other percentages of the ***thiol*** ester total side chains that include sulfur are disclosed herein.

DETD In some embodiments, the process for producing a ***thiol*** ester composition includes contacting an unsaturated ester and hydrogen sulfide and reacting the unsaturated ester and the hydrogen sulfide to form a ***thiol*** ester. The ***thiol*** ester comprises ***thiol*** ester molecules that have a ratio of cyclic sulfide to ***thiol*** groups of less than 1.5.

DETD ***Thiol*** Ester from a Polyol and a ***Thiol*** Containing Carboxylic Acid Derivative

DETD As another embodiment of the present invention, another process to produce the ***thiol*** ester composition is advantageously provided. In this embodiment, the process includes the steps of contacting a composition comprising a polyol with a composition comprising a ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative and reacting the polyol and ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative to produce the ***thiol*** ester composition. This process can be applied to any polyol, ***thiol*** containing carboxylic acid, or ***thiol***

containing carboxylic acid derivative described herein. The process for producing the ***thiol*** ester composition can also include any additional process steps or process conditions described herein. Additionally, the process for producing the ***thiol*** ester composition can form any ***thiol*** ester described herein.

DETD In some embodiments, the ***thiol*** ester composition includes ***thiol*** ester molecules that have an average of at least 1.5 ester groups and an average of at least 1.5 ***thiol*** groups per ***thiol*** ester molecule.

DETD The polyol used to produce the ***thiol*** ester by contacting a polyol and a ***thiol*** carboxylic acid and/or ***thiol*** carboxylic acid equivalent (for example a ***thiol*** carboxylic acid methyl ester) can be any polyol or mixture of polyols that can produce the described ***thiol*** containing ester.

DETD In one aspect, the polyol used to produce the ***thiol*** ester can comprise from 2 to 20 carbon atoms. In other embodiments, the polyol comprises from 2 to 10 carbon atoms; alternatively from 2 to 7 carbon atoms; alternatively from 2 to 5 carbon atoms. In further embodiments, the polyol may be a mixture of polyols having an average of 2 to 20 carbon atoms; alternatively, an average of from 2 to 10 carbon atoms; alternatively, an average of 2 to 7 carbon atoms; alternatively an average of 2 to 5 carbon atoms.

DETD In another aspect, the polyol used to produce the ***thiol*** ester can have any number of hydroxy groups needed to produce the ***thiol*** ester as described herein. In some embodiments, the polyol has 2 hydroxy groups; alternatively 3 hydroxy groups; alternatively, 4 hydroxy groups; alternatively, 5 hydroxy groups; or alternatively, 6 hydroxy groups. In other embodiments, the polyol comprises at least 2 hydroxy groups; alternatively at least 3 hydroxy groups; alternatively, at least 4 hydroxy groups; or alternatively, at least 5 hydroxy groups; at least 6 hydroxy groups. In yet other embodiments, the polyol comprises from 2 to 8 hydroxy groups; alternatively, from 2 to 4 hydroxy groups; or alternatively from 4 to 8 hydroxy groups.

DETD In further aspects, the polyol used to produce the ***thiol*** ester is a mixture of polyols. In an embodiment, the mixture of polyols has an average of at least 1.5 hydroxy groups per polyol molecule. In

other embodiments, the mixture of polyols has an average of at least 2 hydroxy groups per polyol molecule; alternatively, an average of at least 2.5 hydroxy groups per polyol molecule; alternatively, an average of at least 3.0 hydroxy groups per polyol molecule; or alternatively, an average of at least 4 hydroxy groups per polyol molecule. In yet another embodiments, the mixture of polyols has an average of 1.5 to 8 hydroxy groups per polyol molecule; alternatively, an average of 2 to 6 hydroxy groups per polyol molecule; alternatively, an average of 2.5 to 5 hydroxy groups per polyol molecule; alternatively, an average of 3 to 4 hydroxy groups per polyol molecule; alternatively, an average of 2.5 to 3.5 hydroxy groups per polyol molecule; or alternatively, an average of 2.5 to 4.5 hydroxy groups per polyol molecule.

DETD In yet another aspect, the polyol or mixture of polyols used to produce the ***thiol*** ester has a molecular weight or average molecular weight less than 500. In other embodiments, the polyol or mixture of polyols have a molecular weight or average molecular weight less than 300; alternatively less than 200; alternatively, less than 150; or alternatively, less than 100.

DETD The ***thiol*** carboxylic acid and/or ***thiol*** carboxylic acid equivalent used to produce the ***thiol*** ester by contacting a polyol and a ***thiol*** carboxylic acid and/or ***thiol*** carboxylic acid equivalent can be any ***thiol*** carboxylic acid mixture comprising ***thiol*** carboxylic acids, ***thiol*** carboxylic acid equivalent or mixture comprising ***thiol*** carboxylic acid equivalents that can produce the described ***thiol*** containing ester. When talking about the characteristics ***thiol*** carboxylic acid equivalent or ***thiol*** carboxylic acid equivalents, properties such as number of carbon atoms, average number of carbon atom, molecular weight or average molecular weight, number of ***thiol*** group, and average number of ***thiol*** groups, one will understand the these properties will apply to the portion of the ***thiol*** carboxylic acid equivalent which adds to the polyol to form the ***thiol*** ester.

DETD In an aspect, the ***thiol*** carboxylic acid and/or ***thiol*** carboxylic acid equivalent used to produce the ***thiol*** ester comprises from 2 to 28 carbon atoms. In an embodiment, the ***thiol*** carboxylic acid and/or ***thiol*** carboxylic acid equivalent comprises from 4 to 26 carbon atoms; alternatively, from 8 to 24 carbon atoms; alternatively, from 12 to 24 carbon atoms; or alternatively, from 14 to 20 carbon atoms. In other embodiments, a mixture comprising ***thiol*** carboxylic acid and/or mixture comprising ***thiol*** carboxylic acid equivalents has an average of 2 to 28 carbon atoms per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 4 to 26 carbon atoms per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 8 to 24 carbon atoms per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 12 to 24 carbon atoms per carboxylic acid and/or carboxylic acid equivalent; or alternatively, from 14 to 20 carbon atoms per carboxylic acid and/or carboxylic acid equivalent.

DETD In another aspect, the ***thiol*** carboxylic acid and/or ***thiol*** carboxylic acid equivalent used to produce the ***thiol*** ester has at least 1 ***thiol*** group; alternatively 2 ***thiol*** groups. In some embodiments, a mixture comprising ***thiol*** carboxylic acid and/or mixture comprising ***thiol*** carboxylic acid equivalents has an average of from 0.5 to 3 ***thiol*** groups per carboxylic acid and/or carboxylic acid equivalent; alternatively, an average of from 1 to 2 ***thiol*** groups per carboxylic acid and/or carboxylic acid equivalent.

DETD In another aspect, the ***thiol*** carboxylic acid and/or ***thiol*** carboxylic acid equivalent used to produce the ***thiol*** ester has a molecular weight greater than 100; alternatively greater than 180; alternatively greater than 240; or alternatively greater than 260. In other embodiments, the ***thiol*** carboxylic acid and/or ***thiol*** carboxylic acid equivalent has a molecular weight from 100 to 500; alternatively, from 120 to 420; alternatively, from 180 to 420; alternatively, from 240 to 420; a mixture or alternatively, from 260 to 360. In some embodiments, a mixture comprising ***thiol*** carboxylic acid and/or mixture comprising ***thiol*** carboxylic acid equivalents has an average molecular weight greater than 100 per carboxylic acid and/or carboxylic acid equivalent; alternatively greater than 180 per carboxylic acid and/or carboxylic acid equivalent; alternatively greater than 240

per carboxylic acid and/or carboxylic acid equivalent; or alternatively greater than 260 per carboxylic acid and/or carboxylic acid equivalent.

In yet other embodiments, the mixture comprising of ***thiol*** carboxylic acid and/or mixture comprising ***thiol*** carboxylic acid equivalents has an average molecular weight from 100 to 500 per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 120 to 420 per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 180 to 420 per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 240 to 420 per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 260 to 360 per carboxylic acid and/or carboxylic acid equivalent.

DETD In some aspects, the reaction between the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative occurs in the presence of a solvent. In other aspects the reaction between the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative occurs in the substantial absence of a solvent. In aspects wherein the reaction between the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative occurs in the presence of a solvent, the solvent is selected from the group consisting of an aliphatic hydrocarbon, an ether, an aromatic compound, or any combination thereof.

Generally, the solvent, regardless of its chemical class, can include from 1 to 20 carbon atoms; or alternatively, from 3 to 10 carbon atoms. When the solvent includes the aliphatic hydrocarbon, the aliphatic hydrocarbon is butane, isobutane, pentane, hexane, heptane, octane, or any mixture thereof. When the solvent includes the aromatic compound, the aromatic compound is benzene, toluene, xylene, ethylbenzene, or any mixture thereof. When the solvent includes the ether, the ether is diethyl ether, dipropyl ether, tetrahydrofuran, and any mixture thereof.

DETD When a solvent is used for the reaction between the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative, the quantity of solvent can be

any amount that facilitates the reaction. In some embodiments, the mass of the solvent is less than 30 times the mass of the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative. In other embodiments, the mass of the solvent is less than 20 times the mass of the unsaturated ester oil; alternatively, less than 15 times the mass of the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative; alternatively, less than 10 times the mass of the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative; or alternatively, less than 5 times the mass of the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative. In other embodiments, the mass of the solvent is from 2 times to 20 times the mass of the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative; alternatively, from 3 times to 15 times the mass of the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative, or alternatively, from 5 times to 10 times the mass of the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative. DETD The equivalent of ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative carboxylic acid groups to equivalents of polyol hydroxy groups molar ratio (hereinafter "carboxylic acid group to polyol hydroxy group molar ratio") utilized in the process to produce the ***thiol*** ester composition can be any carboxylic acid group to polyol hydroxy group molar ratio that produces the desired ***thiol*** ester composition. In some embodiments, the carboxylic acid group to polyol hydroxy group molar ratio is greater than 0.4. In other embodiments, the carboxylic acid group to polyol hydroxy group molar ratio is greater than 0.6; alternatively, greater than 0.8; alternatively, greater than 1; or alternatively, greater than 1.1. In other embodiments, the carboxylic acid group to polyol hydroxy group molar ratio can range from 0.4 to 1.3; alternatively, from 0.6 to 1.2, or alternatively, from 0.8 to 1.1.

DETD In some aspects, the reaction between the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative is catalyzed. In some embodiments, the catalyst is a mineral acid, such as sulfuric or phosphoric acid. In other embodiments, the catalyst is an organic acid. In embodiments, for example, the organic acid is methane sulfonic acid or toluene sulfonic acid. Other suitable types of catalyst will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD The reaction of the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative can occur in a batch reactor or a continuous reactor, as described herein. The reaction between the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative can be performed at any temperature capable of forming the ***thiol*** ester. In some embodiments, the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative can be reacted at a temperature greater than 20.degree. C. In other embodiments, the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative can be reacted at a temperature greater than 50.degree. C.; alternatively, greater than 75.degree. C.; or alternatively, greater than 100.degree. C. In yet other embodiments, the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative can be reacted at a temperature from 20.degree. C. to 250.degree. C.; alternatively, from 50.degree. C. to 200.degree. C.; alternatively, from 75.degree. C. to 175.degree. C.; or alternatively, from 100.degree. C. to 150.degree. C.

DETD The time required for the reaction of the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative can be any time required to form the described ***thiol*** ester oil. Generally, the reaction time of the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative is at least 5 minutes. In some

embodiments, the reaction time is at least 30 minutes; alternatively, at least 1 hour; or alternatively, at least 2 hours. In yet other embodiments, the reaction time ranges from 5 minutes to 72 hours; alternatively, from 30 minutes to 48 hours; alternatively, from 1 hour minutes to 36 hours; or alternatively, from 2 hours and 24 hours.

DETD When a continuous reactor is used, a feed polyol weight unsaturated ester weight hourly space velocity ranging from 0.1 to 5 can be used to produce the desired ***thiol*** ester. Alternatively, the feed polyol weight hourly space velocity ranges between 0.1 to 5; alternatively, from 0.1 to 2. Alternatively, the feed polyol ester weight hourly space velocity is 0.1; alternatively, the feed polyol weight hourly space velocity is 0.25; or alternatively, the feed polyol weight hourly space velocity is 2.

DETD The reaction between the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative can be performed at any reaction pressure that maintains the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative in a liquid state.

In some embodiments, the reaction between the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative is performed at a pressure ranging from 0 psia to 2000 psia. In other embodiments, the reaction pressure ranges from 0 psia to 1000 psia; alternatively, from 0 psia and 500 psia; or alternatively, 0 psia to 300 psia.

DETD In some embodiments, the process to produce the ***thiol*** ester by reacting a polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative can further include a step to remove excess or residual polyol, ***thiol*** containing carboxylic acid, and/or ***thiol*** containing carboxylic acid derivative once the polyol has reacted with the ***thiol*** containing carboxylic acid or ***thiol*** containing carboxylic acid derivative. In some embodiments, the ***thiol*** ester is vacuum stripped. In some embodiments, the ***thiol*** ester is vacuum stripped at a temperature ranging between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the ***thiol*** ester is sparged with an inert

gas to remove excess polyol, ***thiol*** containing carboxylic acid, and/or ***thiol*** containing carboxylic acid derivative. In some embodiments, the ***thiol*** ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged ***thiol*** ester comprises less than 5 excess polyol, ***thiol*** containing carboxylic acid, or ***thiol*** containing carboxylic acid derivative. In other embodiments, the stripped or sparged ***thiol*** ester comprises less than 2 weight percent excess polyol, ***thiol*** containing carboxylic acid, and/or ***thiol*** containing carboxylic acid derivative; alternatively, less than 1 weight percent excess polyol, ***thiol*** containing carboxylic acid, and/or ***thiol*** containing carboxylic acid derivative; or alternatively, less than 0.5 weight percent excess polyol, ***thiol*** containing carboxylic acid, and/or ***thiol*** containing carboxylic acid derivative.

DETD Process for Making Hydroxy ***Thiol*** Ester Composition
DETD The present invention advantageously provides processes for producing a hydroxy ***thiol*** ester as embodiments of the present invention.

As an embodiment, the present invention includes a process to produce the hydroxy ***thiol*** ester. The process comprises the steps of contacting hydrogen sulfide and an epoxidized unsaturated ester composition and reacting the hydrogen sulfide and the epoxidized unsaturated ester to form the hydroxy ***thiol*** ester. As another embodiment of the present invention, another process to produce the hydroxy ***thiol*** ester is provided. In this embodiment, the process comprises the steps of contacting a composition comprising a polyol with a composition comprising an hydroxy ***thiol*** containing carboxylic acid or an hydroxy ***thiol*** containing carboxylic acid derivative and reacting the polyol and the hydroxy ***thiol*** containing carboxylic acid or the hydroxy ***thiol*** containing carboxylic acid derivative to form the hydroxy ***thiol*** ester.

DETD Hydroxy ***Thiol*** Ester from Hydrogen Sulfide and an Epoxidized

Unsaturated Ester Composition

DETD As an embodiment of the present invention, the hydroxy ***thiol*** ester composition is produced by a process comprising the steps of

contacting hydrogen sulfide and an epoxidized unsaturated ester composition and reacting the hydrogen sulfide and the epoxidized unsaturated ester to produce the hydroxy ***thiol*** ester composition.

DETD In some embodiments, the epoxidized unsaturated ester composition includes epoxidized unsaturated esters that have an average of at least 1 ester groups and an average of at least 1 ***epoxide*** groups per epoxidized unsaturated ester molecule.

DETD The process for producing or preparing the hydroxy ***thiol*** ester composition can be applied to any of the epoxidized unsaturated esters described herein and used to produce any hydroxy ***thiol*** ester described herein. The process for producing the hydroxy ***thiol*** ester can also include any additional process steps or process conditions as described herein. Additionally, the process for producing the hydroxy ***thiol*** ester can form any hydroxy ***thiol*** ester described herein.

DETD In some aspects, the hydroxy ***thiol*** ester is produced by

contacting hydrogen sulfide with the epoxidized natural source oil under the reaction conditions to form the hydroxy ***thiol*** ester in the presence of an optional catalyst. In some embodiments, the catalyst can be a heterogeneous catalyst or a homogeneous catalyst. Examples of suitable catalysts are described herein. Additional types of suitable catalysts will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD The hydrogen sulfide to molar equivalents of ***epoxide*** groups in the epoxidized unsaturated ester (hereinafter "hydrogen sulfide to ***epoxide*** group molar ratio") utilized in the process to produce the hydroxy ***thiol*** ester can be any hydrogen sulfide to ***epoxide*** group molar ratio that produces the desired hydroxy ***thiol*** ester. The molar equivalents of epoxidized unsaturated ester epoxidized groups can be calculated by the equation:

##EQU2##

In this equation, EUES GMW is the average gram molecular weight of the epoxidized unsaturated ester, EUES Mass is the mass of the epoxidized

unsaturated ester, and EUES ***Epoxide*** is the average number of ***epoxide*** groups per epoxidized unsaturated ester molecule. In some embodiments, the hydrogen sulfide to ***epoxide*** group molar ratio is greater than 0.2. In other embodiments, the hydrogen sulfide to ***epoxide*** group molar ratio is greater than 0.5; alternatively, greater than 1; or alternatively, greater than 2. In other embodiments, the hydrogen sulfide to ***epoxide*** group molar ratio ranges from 0.2 to 5; alternatively, from 0.5 to 4; or alternatively, from 0.75 to 3. In some embodiments, the hydrogen sulfide to ***epoxide*** group molar ratio is greater than 2. In other embodiments, the hydrogen sulfide to ***epoxide*** group molar ratio is greater than 5; alternatively, greater than 10; alternatively, greater than 15; or alternatively, greater than 20. In other embodiments, the hydrogen sulfide to ***epoxide*** group molar ratio can be from 0.2 to 500; alternatively, from 0.5 to 400; alternatively, from 1 to 300; alternatively, from 2 to 250; alternatively, 5 to 200; or alternatively, from 10 to 100.

DETD The time required for the reaction of the epoxidized unsaturated ester and hydrogen sulfide can be any time required to form the described hydroxy ***thiol*** ester. Generally, the time required for the reaction of the epoxidized unsaturated ester and hydrogen sulfide is at least 15 minutes. In some embodiments, the time required for the reaction of the unsaturated ester and hydrogen sulfide ranges from 15 minutes to 72 hours; alternatively, from 30 minutes to 48 hours; alternatively, from 45 minutes to 36 hours.

DETD In some embodiments, the hydroxy ***thiol*** ester composition includes hydroxy ***thiol*** ester molecules that have an average of greater than 2.5 weight percent ***thiol*** sulfur. In some embodiments, the hydroxy ***thiol*** ester composition includes hydroxy ***thiol*** ester molecules that have an average of greater than 5 weight percent ***thiol*** sulfur. Alternatively, in some embodiments, the hydroxy ***thiol*** ester molecules have an average ranging from 8 to 10 weight percent ***thiol*** sulfur.

DETD In other aspects, the process producing the hydroxy ***thiol*** ester composition includes producing hydroxy ***thiol***

ester molecules having an average of greater than 40 percent of the sulfide-containing ester total side chains comprise a sulfide group. Additional embodiments wherein the hydroxy ***thiol*** ester comprises a percentage of sulfide-containing ester total side chains are described herein.

DETD In embodiments, the process to produce the hydroxy ***thiol*** ester further comprises a step to remove residual hydrogen sulfide after reacting the hydrogen sulfide and the epoxidized unsaturated ester composition. In some embodiments, the hydroxy ***thiol*** ester is vacuum stripped. In some embodiments, the hydroxy ***thiol*** ester is vacuum stripped at a temperature ranging between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the hydroxy ***thiol*** ester is sparged with an inert gas to remove hydrogen sulfide. In some embodiments, the hydroxy ***thiol*** ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged hydroxy ***thiol*** ester comprises less than 0.1 weight percent hydrogen sulfide. In other embodiments, the stripped or sparged hydroxy ***thiol*** ester comprises less than 0.05 weight percent hydrogen sulfide; alternatively, less than 0.025 weight percent hydrogen sulfide; or alternatively, less than 0.01 weight percent hydrogen sulfide.

DETD The reaction between the hydrogen sulfide and the epoxidized unsaturated ester can be performed at any temperature capable of forming the hydroxy ***thiol*** ester. In some embodiments, the epoxidized unsaturated ester and hydrogen sulfide can be reacted at a reaction temperature greater than -20.degree. C. In other embodiments, the reaction temperature is greater than 0.degree. C.; alternatively, greater than 20.degree. C.; alternatively, greater than 50.degree. C.; or alternatively, greater than 80.degree. C. In yet other embodiments, the reaction temperature ranges from -20.degree. C. to 200.degree. C.; alternatively, from 20.degree. C. to 170.degree. C.; or alternatively, from 80.degree. C. to 140.degree. C.

DETD In another aspect, the process to produce a hydroxy

thiol ester produces a hydroxy ***thiol*** ester having an ***epoxide*** group to ***thiol*** group molar ratio less than 3.3. In another aspect, the process to produce a hydroxy ***thiol*** ester produces a hydroxy ***thiol*** ester having an ***epoxide*** group to ***thiol*** group molar ratio less than 2. Other hydroxy ***thiol*** ester ***epoxide*** group to ***thiol*** group molar ratios are described herein. Alternatively, the hydroxy ***thiol*** ester ***epoxide*** group to ***thiol*** group molar ratio can be less than 1.5; alternatively, less than 1.0; alternatively, less than 0.5; alternatively, less than 0.25; or alternatively, less than 0.1. In other embodiments, the hydroxy ***thiol*** ester can be substantially free of ***epoxide*** groups.

DETD In another aspect, the process to produce hydroxy ***thiol*** ester produces a hydroxy ***thiol*** ester wherein at least 20 percent of the side chains comprise an .alpha.-hydroxy ***thiol*** group. Other hydroxy ***thiol*** ester embodiments wherein the hydroxy ***thiol*** ester contains a percentage of side chains comprising .alpha.-hydroxy ***thiol*** groups are described herein.

DETD Hydroxy ***Thiol*** Ester from a Polyol and a Hydroxy ***Thiol*** Containing Carboxylic Acid Derivative

DETD As another embodiment of the present invention, another process to prepare the hydroxy ***thiol*** ester is advantageously provided. In this embodiment, the process includes the steps of contacting a composition comprising a polyol with a composition comprising a hydroxy ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative and reacting the polyol and hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid to form a hydroxy ***thiol*** ester composition. This process can be applied to any polyol, any hydroxy ***thiol*** containing carboxylic acid, or any ***thiol*** containing carboxylic acid derivative described herein. The process for producing the hydroxy ***thiol*** ester composition can also include any additional process steps or process conditions described herein. Additionally, the process for producing the hydroxy ***thiol*** ester composition can form any ***thiol*** ester described

herein.

DETD In some embodiments, the hydroxy ***thiol*** ester composition includes hydroxy ***thiol*** ester molecules that have an average of at least 1 ester groups per hydroxy ***thiol*** ester molecule and

an average of at least 1 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule.

DETD The polyol used to produce the hydroxy ***thiol*** ester by contacting a polyol and a hydroxy ***thiol*** carboxylic acid and/or

hydroxy ***thiol*** carboxylic acid equivalent (for example a hydroxy ***thiol*** carboxylic acid methyl ester) can be any polyol or mixture of polyols that can produce the described

thiol containing ester.

DETD In one aspect, the polyol used to produce the hydroxy ***thiol*** ester can comprise from 2 to 20 carbon atoms. In other

embodiments, the polyol comprises from 2 to 10 carbon atoms; alternatively from 2 to 7 carbon atoms; alternatively from 2 to 5 carbon atoms. In further embodiments, the polyol may be a mixture of polyols having an average of 2 to 20 carbon atoms; alternatively, an average of from 2 to 10 carbon atoms; alternatively, an average of 2 to 7 carbon atoms; alternatively

an average of 2 to 5 carbon atoms.

DETD In another aspect, the polyol used to produce the hydroxy ***thiol*** ester can have any number of hydroxy groups needed to produce the hydroxy ***thiol*** ester as described herein. In some

embodiments, the polyol has 2 hydroxy groups; alternatively 3 hydroxy groups; alternatively, 4 hydroxy groups; alternatively, 5 hydroxy groups; or

alternatively, 6 hydroxy groups. In other embodiments, the polyol comprises at least 2 hydroxy groups; alternatively at least 3 hydroxy groups; alternatively, at least 4 hydroxy groups; or

alternatively, at least 5 hydroxy groups; at least 6 hydroxy groups. In yet other embodiments, the polyol comprises from 2 to 8 hydroxy groups; alternatively, from 2 to 4 hydroxy groups; or alternatively from 4 to 8 hydroxy groups.

DETD In further aspects, the polyol used to produce the hydroxy ***thiol*** ester is a mixture of polyols. In an embodiment, the mixture of polyols has an average of at least 1.5 hydroxy groups per

polyol molecule. In other embodiments, the mixture of polyols has an average of at least 2 hydroxy groups per polyol molecule; alternatively,

an average of at least 2.5 hydroxy groups per polyol molecule; alternatively, an average of at least 3.0 hydroxy groups per polyol molecule; or alternatively, an average of at least 4 hydroxy groups per polyol molecule. In yet another embodiments, the mixture of polyols has an average of 1.5 to 8 hydroxy groups per polyol molecule; alternatively, an average of 2 to 6 hydroxy groups per polyol molecule; alternatively, an average of 2.5 to 5 hydroxy groups per polyol molecule; alternatively, an average of 3 to 4 hydroxy groups per polyol molecule; alternatively, an average of 2.5 to 3.5 hydroxy groups per polyol molecule; or alternatively, an average of 2.5 to 4.5 hydroxy groups per polyol molecule.

DETD In yet another aspect, the polyol or mixture of polyols used to produce the hydroxy ***thiol*** ester has a molecular weight or average molecular weight less than 500. In other embodiments, the polyol or mixture of polyols have a molecular weight or average molecular weight less than 300; alternatively less than 200; alternatively, less than 150; or alternatively, less than 100.

DETD The hydroxy ***thiol*** carboxylic acid and/or hydroxy ***thiol*** carboxylic acid equivalent used to produce the hydroxy ***thiol*** ester by contacting a polyol and a hydroxy ***thiol*** carboxylic acid and/or hydroxy ***thiol*** carboxylic acid equivalent can be any hydroxy ***thiol*** carboxylic acid mixture comprising hydroxy ***thiol*** carboxylic acids, hydroxy ***thiol*** carboxylic acid equivalent or mixture comprising hydroxy ***thiol*** carboxylic acid equivalents that can produce the described hydroxy ***thiol*** containing ester. When talking about the characteristics hydroxy ***thiol*** carboxylic acid equivalent or hydroxy ***thiol*** carboxylic acid equivalents, properties such as number of carbon atoms, average number of carbon atom, molecular weight or average molecular weight, number of ***thiol*** group, and average number of ***thiol*** groups, one will understand the these properties will apply to the portion of the ***thiol*** carboxylic acid equivalent which adds to the polyol to form the ***thiol*** ester.

DETD In an aspect, the hydroxy ***thiol*** carboxylic acid and/or hydroxy ***thiol*** carboxylic acid equivalent used to produce the

thiol ester comprises from 2 to 28 carbon atoms. In an embodiment, the hydroxy ***thiol*** carboxylic acid and/or hydroxy ***thiol*** carboxylic acid equivalents comprises from 4 to 26 carbon atoms; alternatively, from 8 to 24 carbon atoms; alternatively, from 12 to 24 carbon atoms; or alternatively, from 14 to 20 carbon atoms.

In other embodiments, a mixture comprising hydroxy ***thiol*** carboxylic acids and/or mixture comprising hydroxy ***thiol*** carboxylic acid equivalents has an average of 2 to 28 carbon atoms per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 4 to 26 carbon per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 8 to 24 carbon atoms per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 12 to 24 carbon atoms per carboxylic acid and/or carboxylic acid equivalent; or alternatively, from 14 to 20 carbon atoms per carboxylic acid and/or carboxylic acid equivalent.

DETD In another aspect, the hydroxy ***thiol*** carboxylic acid and/or hydroxy ***thiol*** carboxylic acid equivalent used to produce the ***thiol*** ester has at least 1 ***thiol*** group, alternatively 2 ***thiol*** groups. In some embodiments, a mixture comprising hydroxy ***thiol*** carboxylic acids and/or mixture comprising hydroxy ***thiol*** carboxylic acid equivalents has an average of from 0.5 to 3 ***thiol*** groups per carboxylic acid and/or carboxylic acid equivalent; alternatively, an average of from 1 to 2 ***thiol*** groups per carboxylic acid and/or carboxylic acid equivalent.

DETD In another aspect, the hydroxy ***thiol*** carboxylic acid and/or hydroxy ***thiol*** carboxylic acid equivalent used to produce the ***thiol*** ester has at least 1 hydroxy group; alternatively, at least 2 hydroxy groups. In some embodiments, a mixture comprising hydroxy ***thiol*** carboxylic acids and/or mixture comprising hydroxy ***thiol*** carboxylic acid equivalents has an average of from 0.5 to 3 hydroxy groups per carboxylic acid and/or carboxylic acid equivalent; alternatively, an average of from 1 to 2 hydroxy groups per carboxylic acid and/or carboxylic acid equivalent.

DETD In another aspect, the hydroxy ***thiol*** carboxylic acid

and/or hydroxy ***thiol*** carboxylic acid equivalent used to produce the hydroxy ***thiol*** ester has a molecular weight greater than 100; alternatively greater than 180; alternatively greater than 240; or alternatively greater than 260. In other embodiments, the hydroxy ***thiol*** carboxylic acid and/or hydroxy ***thiol*** carboxylic acid equivalent has a molecular weight from 100 to 500; alternatively, from 120 to 420; alternatively, from 180 to 420; alternatively, from 240 to 420; a mixture or alternatively, from 260 to 360. In some embodiments, a mixture comprising hydroxy ***thiol*** carboxylic acids and/or mixture comprising hydroxy ***thiol*** carboxylic acid equivalents has an average molecular weight greater than 100 per carboxylic acid and/or carboxylic acid equivalent; alternatively greater than 180 per carboxylic acid and/or carboxylic acid equivalent; alternatively greater than 240 per carboxylic acid and/or carboxylic acid equivalent; or alternatively greater than 260 per carboxylic acid and/or carboxylic acid equivalent. In yet other embodiments, the mixture comprising hydroxy ***thiol*** carboxylic acid and/or mixture comprising hydroxy ***thiol*** carboxylic acid equivalents has an average molecular weight from 100 to 500 per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 120 to 420 per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 180 to 420 per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 240 to 420 per carboxylic acid and/or carboxylic acid equivalent; a mixture or alternatively, from 260 to 360 per carboxylic acid and/or carboxylic acid equivalent.

DETD In some aspects, the reaction between the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative occurs in the presence of a solvent. In other aspects, the reaction between the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative occurs in the substantial absence of a solvent. In aspects wherein the reaction between the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative occurs in the presence of a solvent, the solvent is selected from the group consisting of an aliphatic hydrocarbon, an ether, an aromatic compound, or any combination thereof. Generally, the

solvent,
regardless of its chemical class, includes from 1 to 20 carbon atoms;
alternatively, from 3 to 10 carbon atoms. When the solvent includes the aliphatic hydrocarbon, the aliphatic hydrocarbon is butane, isobutane,
pentane, hexane, heptane, octane, or any mixture thereof. When the solvent includes the aromatic compound, the aromatic compound is benzene, toluene, xylene, ethylbenzene, or any mixture thereof. When the solvent includes the ether, the ether is diethyl ether, dipropyl ether,
tetrahydrofuran, and any mixture thereof.

DETD When a solvent is used for the reaction between the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative, the quantity of solvent can be any amount that facilitates the reaction. In some embodiments, the mass of the solvent is less than 30 times the mass of the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative. In other embodiments, the mass of the solvent is less than 20 times the mass of the hydroxy ***thiol*** ester; alternatively, less than 15 times the mass of the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative; alternatively, less than 10 times the mass of the hydroxy ***thiol*** containing carboxylic acid derivative; or alternatively, less than 5 times the mass of the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative. In other embodiments, the mass of the solvent is from 2 times to 20 times the mass of the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative; alternatively, from 3 times to 15 times the mass of the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative; or alternatively, from 5 times to 10 times the mass of the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative.

DETD The equivalents of hydroxy ***thiol*** containing carboxylic acid derivative and/or hydroxy ***thiol*** containing carboxylic acid

derivative carboxylic acid groups to equivalents of polyol hydroxy groups molar ratio (hereinafter referred to as "carboxylic acid group to polyol hydroxy group molar ratio") utilized in the process to produce the hydroxy ***thiol*** ester can be any carboxylic acid group to polyol hydroxy group molar ratio that produces the desired hydroxy ***thiol*** ester. In some embodiments, the carboxylic acid group to polyol hydroxy group molar ratio is greater than 0.4. In other embodiments, the carboxylic acid group to polyol hydroxy group molar ratio is greater than 0.6; alternatively, greater than 0.8; alternatively, greater than 1; or alternatively, greater than 1.1. In other embodiments, the carboxylic acid group to polyol hydroxy group molar ratio ranges from 0.4 to 1.3; alternatively, from 0.6 to 1.2, or alternatively, from 0.8 to 1.1.

DETD In some aspects, the reaction between the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative is catalyzed. In some embodiments, the catalyst is a mineral acid, such as sulfuric or phosphoric acid. In other embodiments, the catalyst is an organic acid. In embodiments, for example, the organic acid is methane sulfonic acid or toluene sulfonic acid. Other suitable types of catalyst will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD The reaction of the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative can occur in a batch reactor or a continuous reactor, as described herein. The reaction between the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative can be performed at any temperature capable of forming the hydroxy ***thiol*** ester.

In some embodiments, the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative can be reacted at a temperature greater than 20.degree.

C. In other embodiments, the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative can be reacted at a temperature

greater than 50.degree. C.; alternatively, greater than 75.degree. C.; or alternatively, greater than 100.degree. C. In yet other embodiments, the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative can be reacted at a temperature from 20.degree. C. to 250.degree. C.; alternatively, from 50.degree. C. to 200.degree. C.; alternatively, from 75.degree. C. to 175.degree. C.; or alternatively, from 100.degree. C. to 150.degree..

DETD The time required for the reaction of the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative can be any time required to form the described hydroxy ***thiol*** ester composition. Generally, the reaction time is at least 5 minutes. In some embodiments, the reaction time is at least 30 minutes; alternatively, at least 1 hour; or alternatively, at least 2 hours. In yet other embodiments, the reaction time ranges from 5 minutes to 72 hours; alternatively, from 30 minutes to 48 hours; alternatively, from 1 hour minutes to 36 hours; or alternatively, from 2 hours and 24 hours.

DETD The reaction between the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative can be performed at any reaction pressure that maintains the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative in a liquid state. In some embodiments, the reaction pressure ranges from 0 psia to 2000 psia. In other embodiments, the reaction pressure ranges from 0 psia to 1000 psia; alternatively, from 0 psia and 500 psia; or alternatively, from 0 psia to 300 psia.

DETD In some embodiments, the process to produce the hydroxy ***thiol*** ester composition by reacting a polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative can further include a step to remove excess or residual polyol, hydroxy ***thiol*** containing carboxylic acid, and/or hydroxy ***thiol*** containing carboxylic acid derivative once the polyol has reacted with the hydroxy ***thiol*** containing

acid carboxylic acid or hydroxy ***thiol*** containing carboxylic derivative. In some embodiments, the ***thiol*** ester is vacuum stripped. In some embodiments, the hydroxy ***thiol*** ester is vacuum stripped at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the hydroxy ***thiol*** ester is sparged with an inert gas to remove excess polyol, hydroxy ***thiol*** containing carboxylic acid, and/or hydroxy ***thiol*** containing carboxylic acid derivative. In some embodiments, the hydroxy ***thiol*** ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C., or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged hydroxy ***thiol*** ester oil comprises less than 5 excess polyol, hydroxy ***thiol*** containing carboxylic acid, or hydroxy ***thiol*** containing carboxylic acid derivative. In other embodiments, the stripped or sparged hydroxy ***thiol*** ester oil comprises less than 2 weight percent excess polyol, hydroxy ***thiol*** containing carboxylic acid, and/or hydroxy ***thiol*** containing carboxylic acid derivative; less than 1 weight percent excess polyol, hydroxy ***thiol*** containing carboxylic acid, and/or hydroxy ***thiol*** containing carboxylic acid derivative; or alternatively, less than 0.5 weight percent excess polyol, hydroxy ***thiol*** containing carboxylic acid, and/or hydroxy ***thiol*** containing carboxylic acid derivative.

DETD A method of making a thioacrylate containing ester composition is advantageously provided as another embodiment of the present invention.

The process for producing the thioacrylate containing ester comprising contacting a ***thiol*** ester with an acrylate and converting at least one ***thiol*** group to a ***thiol*** acrylate group. The process can be applied to any of the ***thiol*** esters described herein and used to any thioacrylate ester described herein. The process for producing the thioacrylate ester can also include any additional

process steps or process conditions described herein.

DETD The acrylate compound can be any acrylate compound capable of reacting with a ***thiol*** group to form the ***thiol*** acrylate group.

In some embodiments, the acrylate compound can be an acrylic halide. In other embodiments, the acrylate compound can be an acrylic acid. In yet other embodiments, the acrylate compound can be an acrylic anhydride.

DETD In some aspects, the conversion of the ***thiol*** group to a thioacrylate group occurs in the presence of a solvent. In other aspects the conversion of the ***thiol*** group to a thioacrylate group occurs in the substantial absence of a solvent. In aspects wherein the conversion of the ***thiol*** group to a thioacrylate group occurs in the presence of a solvent, the solvent may be an aliphatic hydrocarbon, an ether, and aromatic compound. Generally, the solvent, regardless of its chemical class, includes from 1 to 20 carbon atoms; or alternatively, from 3 to 10 carbon atoms. When the solvent includes the aliphatic hydrocarbon, the aliphatic hydrocarbon is butane, isobutane, pentane, hexane, heptane, octane, or any mixture thereof. When the solvent includes the aromatic compound, the aromatic compound is benzene, toluene, xylene, ethylbenzene, or any mixture thereof.

When the solvent includes the ether, the ether is diethyl ether, dipropyl ether, tetrahydrofuran, or any mixture thereof.

DETD When a solvent is used for the conversion of the ***thiol*** group to a thioacrylate group, the quantity of solvent can be any amount that facilitates the reaction. In some embodiments, the mass of the solvent is less than 30 times the mass of the ***thiol*** ester. In other embodiments, the mass of the solvent is less than 20 times the mass of the ***thiol*** ester; alternatively, less than 15 times the mass of the ***thiol*** ester; alternatively, less than 10 times the mass of the ***thiol*** ester; or alternatively, less than 5 times the mass of the ***thiol*** ester. In other embodiments, the mass of the solvent is from 2 times to 20 times the mass of the ***thiol*** ester; alternatively, from 3 times to 15 times the mass of the ***thiol*** ester; alternatively, 4 times to 15 times the mass of the

thiol ester; or alternatively, from 5 times to 10 times the mass of the ***thiol*** ester.

DETD In some aspects the conversion of the ***thiol*** group to the thioacrylate group occurs in the presence of a catalyst. In some embodiments, the catalyst is homogeneous. In some embodiments, the catalyst is an organic amine. Examples of suitable organic amines include triethylamine, tripropylamine, tributylamine, and pyridine. In other embodiments, the catalyst is heterogeneous. Examples of suitable catalysts include Amberlyst A-21 and Amberlyst A-26. Other suitable catalysts will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD The conversion of the ***thiol*** group to a thioacrylate group can be performed at any conversion temperature that is capable of converting the ***thiol*** group to a thioacrylate group. In some embodiments, the conversion temperature is greater than -20.degree. C. In other embodiments, the conversion temperature is greater than 0.degree. C.; alternatively, greater than 20.degree. C.; alternatively, greater than 50.degree. C.; alternatively, greater than 80.degree. C.; or alternatively, greater than 100.degree. C. In yet other embodiments, the conversion temperature ranges from -20.degree. C. to 250.degree. C.; alternatively, from 20.degree. C. to 200.degree. C.; or alternatively, from 50.degree. C. to 150.degree. C.

DETD The conversion time required for the conversion of the ***thiol*** group to a thioacrylate group can be any time required to form the described thioacrylate containing ester. Generally, the conversion time is at least 5 minutes. In some embodiments, the conversion time is at least 15 minutes; alternatively, at least 30 minutes; alternatively, at least 45 minutes; or alternatively, at least 1 hour. In other embodiments, the conversion time ranges from 15 minutes to 12 hours; alternatively, from 30 minutes to 6 hours; or alternatively, from 45 minutes to 3 hours.

DETD The conversion of the ***thiol*** group to a thioacrylate group can be performed at any conversion pressure that maintains the ***thiol*** ester and the acrylate compound in the liquid state. In some embodiments, the conversion pressure ranges from 0 psia to 2000

psia. In

other embodiments, the conversion pressure ranges from 0 psia to 1000 psia; or alternatively, from 0 psia to 500 psia.

DETD Process for Producing Cross-Linked ***Thiol*** Ester

DETD As an embodiment of the present invention, a process for producing a

cross-linked ***thiol*** ester composition is advantageously provided. Minimally, in some embodiments, the process to produce the

cross-linked ***thiol*** ester composition comprises contacting a

thiol ester composition with an oxidizing agent and reacting the

thiol ester composition and an oxidizing agent to form the

thiol ester oligomer having at least two ***thiol*** ester

monomers connected by a polysulfide linkage having the structure --S._Q--, wherein Q is an integer greater than 1. The disclosed

method may be applied to any ***thiol*** ester described herein to

produce any cross-linked ***thiol*** ester composition as described

herein. The process to produce the cross-linked ***thiol*** ester

composition can also include any additional process steps or process

conditions as described herein.

DETD When elemental sulfur is used as the oxidizing agent, the quantity of

elemental sulfur utilized to form the cross-linked ***thiol*** ester

composition is determined as a function of the ***thiol*** sulfur

content of the ***thiol*** ester composition. In an aspect, the

weight ratio of elemental sulfur to ***thiol*** sulfur in the ***thiol*** ester composition is at least 0.5. In some

embodiments, the weight ratio of elemental sulfur to ***thiol*** sulfur in the

thiol ester composition is at least 5; alternatively, at least

10, alternatively, at least 15, or alternatively, at least 20. In other

embodiments, the weight ratio of elemental sulfur to

thiol

sulfur in the ***thiol*** ester composition ranges from 0.5 to 32;

alternatively, ranges from 1 to 24; alternatively, ranges from 2 to 16;

or alternatively, ranges from 3 to 10.

DETD In an aspect, the reaction of the ***thiol*** ester and

elemental

sulfur occurs in the presence of a catalyst. The catalyst can be any

catalyst that catalyzes the formation of the polysulfide linkage between

at least two ***thiol*** ester monomers. In some embodiments, the catalyst is an amine. In further embodiments, the catalyst is a tertiary amine.

DETD The formation of the cross-linked ***thiol*** ester can occur in a batch reactor or a continuous reactor, as described herein. The formation of the cross-linked ***thiol*** ester can occur at any temperature capable of forming the ***thiol*** ester. In some embodiments, the formation of the cross-linked ***thiol*** ester can occur at a temperature greater than 25.degree. C. In other embodiments, the formation of the cross-linked ***thiol*** ester can occur at a temperature greater than 50.degree. C.; alternatively, greater than 70.degree. C.; or alternatively, greater than 80.degree. C. In yet other embodiments, the formation of the cross-linked ***thiol*** ester occurs at a temperature from 25.degree. C. to 150.degree. C.; alternatively, from 50.degree. C. to 150.degree. C.; alternatively, from 70.degree. C. to 120.degree. C.; or alternatively, from 80.degree. C. to 110.degree. C.

DETD The time required to form the cross-linked ***thiol*** ester can be any time required to form the desired cross-linked ***thiol*** ester. Generally, the time required to form the cross-linked ***thiol*** ester is at least 15 minutes. In some embodiments, the time required to form the cross-linked ***thiol*** ester is at least 30 minutes; alternatively, at least 1 hour; or alternatively, at least 2 hours. In yet other embodiments, the time required to form the cross-linked ***thiol*** ester ranges from 15 minutes to 72 hours; alternatively, from 30 minutes to 48 hours; alternatively, from 1 hour minutes to 36 hours; or alternatively, from 2 hours and 24 hours.

DETD In embodiments, the process to produce the cross-linked ***thiol*** ester further comprises a step to remove residual hydrogen sulfide. In some embodiments the cross-linked ***thiol*** ester is vacuum stripped. In some embodiments, the cross-linked ***thiol*** ester is vacuum striped at a temperature between 25.degree. C. and 250.degree. C.; alternatively, between 50.degree. C. and 200.degree. C.; or alternatively, 75 and 150.degree. C. In some embodiments, the cross-linked ***thiol*** ester oil is sparged with an inert gas to remove residual hydrogen sulfide. In other embodiments, the cross-linked

thiol ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; alternatively, between 50.degree. C. and 200.degree. C.; or alternatively, between 75 and 150.degree. C. In yet other embodiments, the vacuum stripping is performed while sparging the cross-linked ***thiol*** ester with an inert gas. In yet other embodiments, the vacuum stripping is performed while sparging the cross-linked ***thiol*** ester an inert gas at a temperature between 25.degree. C. and 250.degree. C.; alternatively, between 50.degree. C. and 200.degree. C.; or alternatively, 75 and 150.degree. C. In some embodiments, the inert gas is nitrogen.

DETD Generally, the stripped or sparged cross-linked ***thiol*** ester comprises less than 0.1 weight percent hydrogen sulfide. In other embodiments, the stripped or sparged ***thiol*** -containing ester oil comprises less than 0.05 weight percent hydrogen sulfide; alternatively, less than 0.025 weight percent hydrogen sulfide; or alternatively, less than 0.01 weight percent hydrogen sulfide.

DETD The present invention advantageously provides processes for producing sulfide-containing esters as embodiments of the present invention.

Generally, the sulfide-containing esters can be prepared by two processes. As an embodiment of the present invention, the first process used to produce a sulfide-containing ester comprises contacting an unsaturated ester and a ***mercaptan*** and reacting the unsaturated ester and ***mercaptan*** to form a sulfide-containing ester.

As another embodiment of the present invention, the second process used to produce a sulfide-containing ester comprises contacting an epoxidized unsaturated ester and a ***mercaptan*** sulfide and reacting the unsaturated ester and ***mercaptan*** to form a sulfide-containing ester. Additional aspects of the two sulfide-containing ester production processes are described below.

DETD The sulfide-containing esters and sulfide-containing ester compositions described herein can be produced by a process comprising contacting a ***mercaptan*** and an unsaturated ester and reacting the ***mercaptan*** and the unsaturated ester to form a sulfide-containing ester. The process can be applied to any of the unsaturated esters and ***mercaptans*** described herein. The process for producing

the sulfide-containing ester can also include any additional process steps or process conditions described herein. Additionally, the process for producing the sulfide-containing ester can form any sulfide-containing ester described herein.

DETD In some aspects, the reaction between the ***mercaptan*** and the unsaturated ester occurs in the presence of a solvent. In other aspects the reaction between the ***mercaptan*** and the unsaturated ester occurs in the substantial absence of a solvent. When the reaction occurs in the presence of a solvent, the solvent is selected from an aliphatic hydrocarbon, an ether, an aromatic compound, an alcohol, or any combination thereof. Generally, the solvent, regardless of its chemical class, can comprise from 1 to 20 carbon atoms; alternatively, from 3 to 10 carbon atoms. When the solvent includes an aliphatic hydrocarbon, the aliphatic hydrocarbon is butane, isobutane, pentane, hexane, heptane, octane, or any mixture thereof. When the solvent includes an aromatic compound, the aromatic compound is benzene, toluene, xylene, ethylbenzene, or any mixture thereof. When the solvent includes an alcohol, the alcohol is methanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-2-propanol, or any mixture thereof. When the solvent includes an ether, the ether is diethyl ether, dipropyl ether, tetrahydrofuran, or any mixture thereof.

DETD When a solvent is used for the reaction between the ***mercaptan*** and the unsaturated ester, the quantity of solvent can be any amount that facilitates the reaction, as understood by those of skill in the art. In some embodiments, the mass of the solvent is less than 30 times the mass of the unsaturated ester. In other embodiments, the mass of the solvent is less than 20 times the mass of the unsaturated ester; alternatively, less than 15 times the mass of the unsaturated ester; alternatively, less than 10 times the mass of the unsaturated ester; or alternatively, less than 5 times the mass of the unsaturated ester. In other embodiments, the mass of the solvent is from 2 times to 20 times the mass of the unsaturated ester; alternatively, from 3 times to 15 times the mass of the unsaturated ester; alternatively, from 4

times to

15 times the mass of the unsaturated ester; or alternatively, from 5

times to 10 times the mass of the unsaturated ester.

DETD The molar ratio of ***mercaptan*** to molar equivalents of unsaturated ester carbon-carbon double bonds (herein after " ***mercaptan*** to carbon-carbon double bond molar ratio")

utilized in

the process to produce the sulfide-containing ester can be any ***mercaptan*** to carbon-carbon double bond molar ratio that produces

the desired sulfide-containing ester. The molar equivalents of unsaturated ester carbon-carbon double bonds is calculated by the equation: ##EQU3## In this equation, UES GMW is the average

gram

molecular weight of the unsaturated ester, UES Mass is the mass of the

unsaturated ester, and UES C.dbd.C is the average number of double bonds

per unsaturated ester molecule. In some embodiments, the ***mercaptan*** to carbon-carbon double bond molar ratio is greater

than 0.25. In other embodiments, the ***mercaptan*** to carbon-carbon double bond molar ratio is greater than 0.5; alternatively, greater than 0.75; alternatively, greater than 1; alternatively, greater than 1.25; or alternatively, greater than

1.5. In

other embodiments, the ***mercaptan*** to carbon-carbon double bond molar ratio can range from 0.25 to 2; alternatively, from 0.5 to 1.5, or alternatively, from 0.75 to 1.25.

DETD In some aspects the reaction between the ***mercaptan*** and the

unsaturated ester is catalyzed. The reaction of the ***mercaptan***

and the unsaturated ester can be catalyzed by a heterogeneous

catalyst or homogeneous catalyst, as described herein. In some aspects,

the reaction between the ***mercaptan*** and the unsaturated ester is

initiated by a free radical initiator or ultraviolet radiation, as described herein.

DETD The free radical initiator can be any free radical initiator capable of forming free radicals under thermal or light photolysis.

Generally, the free radical initiator is selected from the general class of compounds

having a --N.dbd.N-- group or a --O-- O-- group. Specific classes of

free radical initiators include diazo compounds, dialkyl

peroxides,

hydroperoxides, and peroxy esters. Specific initiators include

azobenzene, 2,2'-azobis(2-methylpropionitrile,

4,4'-azobis(4-cyanovaleric acid), 1,1'-azobis(cyclohexanecarbo-

nitrile),

2,2'-azobis(2methylpropane), 2,2'-azobis(2-methylpropionamidine)

dihydro-

chloride, methylpropionitrile, azodicarboxamide, tert-butyl hydroperoxide, di-tert-butyl peroxide, octylperbenzoate. In some embodiments, the free radical initiated reaction of the ***mercaptan*** and the unsaturated ester is performed at a reaction

temperature within .+- .50.degree. C. of the 1 hour half life of the free radical initiator. In other embodiments, the reaction temperature is

within .+- .25.degree. C. of the 1 hour half life of the free radical

initiator; alternatively, the reaction temperature is within .+- .20.degree. C. of the 1 hour half life of the free radical initiator;

alternatively, the reaction temperature is within .+- .15.degree.

C. of

the 1 hour half life of the free radical initiator; or alternatively,

the reaction temperature is within .+- .10.degree. C. of the 1 hour half

life of the free radical initiator. In embodiments where the free radical initiated reaction of the ***mercaptan*** and the unsaturated ester is initiated by light photolysis, the light can be any

light capable creating free radicals. In some embodiments, the light is

UV radiation. Other sources of light capable of creating free radicals

will be apparent to those of skill in the art and are to be considered

within the scope of the present invention.

DETD In another aspect, the reaction of the ***mercaptan*** and the

unsaturated ester is initiated by UV radiation. In these embodiments,

the UV radiation may be any UV radiation capable of initiating the

reaction of the ***mercaptan*** and the unsaturated ester. In some embodiments, the UV radiation is generated by a medium pressure mercury

lamp.

DETD The reaction of the ***mercaptan*** and the unsaturated ester can

occur in a batch reactor or a continuous reactor. Any of the batch or

continuous reactors described herein can be used in this reaction. Other

suitable reactors will be apparent to those of skill in the art and are

to be considered within the scope of the present invention.

DETD The reaction time for reacting the ***mercaptan*** and the unsaturated ester can be any time required to form the sulfide-containing ester. Generally, the reaction time is at least 5

minutes. In some embodiments, the reaction time ranges from 5 minutes to

72 hours; alternatively, from 10 minutes to 48 hours; or alternatively,

from 15 minutes to 36 hours.

DETD In some embodiments, the process to produce the sulfide-containing ester further comprises a step to remove any residual ***mercaptan*** that remains after reacting the ***mercaptan*** and the unsaturated ester. In some embodiments, the sulfide-containing ester is vacuum stripped to remove the residual ***mercaptan***. In some embodiments, the sulfide-containing ester is vacuum stripped at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the sulfide-containing ester is sparged with an inert gas to remove the residual ***mercaptan***. In some embodiments, the sulfide-containing ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged sulfide-containing ester comprises less than 5 weight percent of the ***mercaptan***. In other embodiments, the stripped or sparged sulfide-containing ester comprises less than 2 weight percent of the ***mercaptan***; alternatively, less than 1 weight percent of the ***mercaptan***; or alternatively, less than 0.5 weight percent of the ***mercaptan***.

DETD The reaction between the ***mercaptan*** and the unsaturated ester can be performed at any temperature capable of forming the sulfide-containing ester. In some embodiments, the ***mercaptan*** and the unsaturated ester can be reacted at a reaction temperature of greater than -20.degree. C. In other embodiments, the reaction temperature is greater than 0.degree. C.; alternatively, greater than 20.degree. C.; alternatively, greater than 50.degree. C.; alternatively, greater than 80.degree. C.; or alternatively, greater than 100.degree. C. In yet other embodiments, the ***mercaptan*** and the unsaturated ester can be reacted at a temperature from -20.degree. C. to 250.degree. C.; alternatively, from 20.degree. C. to 200.degree. C.; or alternatively, from 80.degree. C. to 160.degree. C.

DETD The reaction between the ***mercaptan*** and the unsaturated ester can be performed at any pressure that maintains the ***mercaptan*** and the unsaturated ester in a substantially liquid state. In

some embodiments, the ***mercaptan*** and the unsaturated ester can be performed at a reaction pressure ranging from 0 psig to 2000 psig. In other embodiments, the reaction pressure ranges from 0 psig to 1000 psig; alternatively, from 0 psig to 500 psig; or alternatively, from 0 psig to 200 psig.

DETD Using the disclosed process, sulfide-containing ester hazing a low carbon-carbon double bond to sulfide group molar ratio can be produced.

In an aspect, the process for producing the sulfide-containing ester forms a sulfide-containing ester having a carbon-carbon double bond to ***thiol*** group molar ratio of less than 1.5. Additional carbon-carbon double bond to sulfide group molar ratios are disclosed herein.

DETD As another embodiment of the present invention, another process for producing a class of sulfide-containing esters, which includes hydroxy sulfide-containing esters, is advantageously provided. In this embodiment, the hydroxy sulfide-containing esters and hydroxy sulfide-containing ester compositions can be produced by a process comprising the steps of contacting a ***mercaptan*** and an epoxidized unsaturated ester and reacting the ***mercaptan*** and the epoxidized unsaturated ester to produce or form the hydroxy sulfide-containing ester. The process can be applied to any ***mercaptan*** and/or any epoxidized unsaturated esters described herein. The process for producing the hydroxy sulfide-containing ester can also include any additional process steps or process conditions as described herein. Additionally, the process for producing the hydroxy sulfide-containing ester can form any hydroxy sulfide-containing ester as described herein.

DETD In some aspects, the reaction between the ***mercaptan*** and the unsaturated ester occurs in the presence of a solvent. In other aspects the reaction between the ***mercaptan*** and the unsaturated ester occurs in the substantial absence of a solvent. When the reaction occurs in the presence of a solvent, the solvent is selected from an aliphatic hydrocarbon, an ether, an aromatic compound, or any combination thereof.

Generally, the solvent, regardless of its chemical class, can comprise

from 1 to 20 carbon atoms; alternatively, from 3 to 10 carbon atoms.

When the solvent includes an aliphatic hydrocarbon, the aliphatic hydrocarbon is butane, isobutane, pentane, hexane, heptane, octane, or any mixture thereof. When the solvent includes an aromatic compound, the aromatic compound is benzene, toluene, xylene, ethylbenzene, or any mixture thereof. When the solvent includes an ether, the ether is diethyl ether, dipropyl ether, tetrahydrofuran, or any mixture thereof.

DETD When a solvent is used for the reaction between the ***mercaptan*** and the epoxidized unsaturated ester, the quantity of solvent can be any amount that facilitates the reaction, as understood by those of skill in the art. In some embodiments, the mass of the solvent is less than 30 times the mass of the epoxidized unsaturated ester. In other embodiments, the mass of the solvent is less than 20 times the mass of the epoxidized unsaturated ester; alternatively, less than 15 times the mass of the epoxidized unsaturated ester; alternatively, less than 10 times the mass of the epoxidized unsaturated ester; or alternatively, less than 5 times the mass of the epoxidized unsaturated ester.

In other embodiments, the mass of the solvent is from 2 times to 20 times the mass of the epoxidized unsaturated ester; alternatively, from 3 times to 15 times the mass of the epoxidized unsaturated ester; alternatively, from 4 times to 15 times the mass of the epoxidized unsaturated ester; or alternatively, from 5 times to 10 times the mass of the epoxidized unsaturated ester.

DETD The reaction of the ***mercaptan*** and the epoxidized unsaturated ester can occur using any ***mercaptan*** to molar equivalents of ***epoxide*** groups in the epoxidized unsaturated ester (hereinafter referred to as " ***mercaptan*** to ***epoxide*** group molar ratio") that is capable of producing the herein described .alpha.-hydroxy ***thiol*** esters. The molar equivalents of epoxidized unsaturated ester epoxidized groups can be calculated by the

equation: ##EQU4##

DETD In this equation, EUES GMW is the average gram molecular weight of the epoxidized unsaturated ester, EUES Mass is the mass of the epoxidized unsaturated ester, and EUES ***Epoxide*** is the average

number of

 epoxide groups per epoxidized unsaturated ester molecule. In some embodiments, the ***mercaptan*** to ***epoxide*** group

 molar ratio is greater than 0.2. In other embodiments, the ***mercaptan*** to ***epoxide*** group molar ratio is greater than 0.5; alternatively, greater than 1; or alternatively, greater than 2. In other embodiments, the hydrogen sulfide to ***epoxide*** group molar

 ratio ranges from 0.2 to 10; alternatively, from 0.5 to 8; alternatively, from 0.75 to 5; or alternatively, from 1 to 3.

DETD In some aspects, the reaction of the ***mercaptan*** and the epoxidized unsaturated ester occurs in the presence of a catalyst.

Generally, the catalyst is any catalyst that is capable of catalyzing

 the reaction of the ***mercaptan*** and the epoxidized unsaturated

 ester to produce the desired hydroxy ***thiol*** ester. In one aspect, the catalyst is selected from the group consisting of homogeneous and heterogeneous catalysts. In other aspects, the catalyst

 is selected from the group consisting of zeolites, heterogeneous catalysts, homogeneous catalysts, and mixtures thereof. In another

 aspect, the catalyst is an amine. In other aspects, the catalyst is selected from the group consisting of cyclic conjugated amines, 1,8-diazabicyclo[5.4.0]undec-7-ene, 1,5-diazabicyclo[4.3.0]non-5-ene,

 and mixtures thereof.

DETD In some aspects, the reaction of the ***mercaptan*** and the epoxidized unsaturated ester occurs in the presence of a catalyst.

Generally, the catalyst is any catalyst that is capable of catalyzing

 the reaction of the ***mercaptan*** and the epoxidized unsaturated

 ester to produce the desired hydroxy ***thiol*** ester. In some

 embodiments the catalyst is an organic base. In some embodiments, the

 catalyst can be 1,8-diazabicyclo[5.4.0]undec-7-ene. (What other catalysts may be used?)

DETD The reaction of the ***mercaptan*** and the epoxidized unsaturated

 ester can occur in a batch reactor or a continuous reactor. Any of the

 batch or continuous reactors described herein can be used in this reaction. Other suitable reactors will be apparent to those of

 skill in

 the art and are to be considered within the scope of the present invention.

DETD The time required for the reaction of the ***mercaptan*** and the

 epoxidized unsaturated ester can be any reaction time required to

form the described hydroxy sulfide-containing ester. Generally, the reaction time is at least 15 minutes. In some embodiments, the reaction time ranges from 15 minutes to 72 hours; alternatively, from 30 minutes to 48 hours; or alternatively, from 45 minutes to 36 hours.

DETD In some embodiments, the process to produce the hydroxy sulfide-containing ester further comprises a step to remove the residual ***mercaptan*** after reacting the ***mercaptan*** and the epoxidized unsaturated ester. In some embodiments the hydroxy sulfide-containing ester is vacuum stripped. In some embodiments, the hydroxy sulfide-containing ester is vacuum stripped at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the hydroxy sulfide-containing ester is sparged with an inert gas to remove the ***mercaptan***. In some embodiments, the hydroxy sulfide-containing ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged hydroxy sulfide-containing ester comprises less than 5 weight percent of the ***mercaptan***. In other embodiments, the stripped or sparged hydroxy sulfide-containing ester comprises less than 2 weight percent of the ***mercaptan***; alternatively, less than 1 weight percent of the ***mercaptan***; or alternatively, less than 0.5 weight percent of the ***mercaptan***.

DETD The reaction between the ***mercaptan*** and the epoxidized unsaturated ester can be performed at any reaction temperature capable of forming the hydroxy sulfide-containing ester. In some embodiments, the reaction temperature is greater than -20.degree. C. In other embodiments, the reaction temperature is greater than 0.degree. C.; alternatively, greater than 20.degree. C.; alternatively, greater than 50.degree. C.; or alternatively, greater than 80.degree. C. In yet other embodiments, the reaction temperature ranges from -20.degree. C. to 200.degree. C.; alternatively, from 20.degree. C. to 170.degree. C.; or alternatively, from 80.degree. C. to 140.degree. C.

DETD The reaction between the ***mercaptan*** and the epoxidized unsaturated ester can be performed at any reaction pressure that maintains the ***mercaptan*** and the epoxidized unsaturated ester in a substantially liquid state. In some embodiments, the reaction

pressure ranges from 0 psig to 2000 psig. In other embodiments, the reaction pressure ranges from 0 psig to 1000 psig; alternatively, from 0

psig to 500 psig; or alternatively, from 0 psig to 200 psig.

DETD In another aspect, the process to produce a hydroxy sulfide-containing ester produces a hydroxy sulfide-containing ester having an ***epoxide*** group to sulfide group molar ratio less than 2.

Other hydroxy sulfide-containing ester ***epoxide*** group to sulfide group molar ratios are described herein. (The next passage needs to be incorporated into the hydroxy ***thiol*** ester section along with

the first sentence of this paragraph.) Alternatively, the hydroxy sulfide-containing ester ***epoxide*** group to ***thiol*** group molar ratio can be less than 1.5; alternatively, less than 1.0;

alternatively, less than 0.5, alternatively, less than 0.25; or alternatively, less than 0.1. In other embodiments, the hydroxy sulfide-containing ester can be substantially free of ***epoxide*** groups.

DETD As an embodiment of the present invention, processes for producing a sulfonic acid-containing ester and for producing a sulfonate-containing

ester are advantageously provided. Generally, the process for producing the sulfonic acid-containing ester comprises the steps of contacting a

thiol ester and an oxidizing agent and oxidizing at least one ***thiol*** group of the ***thiol*** ester to produce a sulfonic

acid group. The process for producing the sulfonate-containing ester

comprises the steps of contacting a sulfonic acid-containing ester with a base and forming a sulfonate-containing ester.

DETD In an embodiment, the process to prepare a sulfonic acid-containing ester comprises the steps of contacting the ***thiol*** ester and

the oxidizing agent and oxidizing the ***thiol*** ester to produce the sulfonic acid-containing ester. Generally the oxidizing agent oxidizes at least one ***thiol*** group of the ***thiol*** ester

to a sulfonate group. The process to produce the sulfonic acid-containing ester composition can be applied to any ***thiol***

ester described herein to prepare any sulfonic acid-containing ester described herein. In some embodiments, the ***thiol*** ester includes a hydroxy group. For example, the ***thiol*** ester can be any hydroxy ***thiol*** ester described herein. The oxidizing agent can be any oxidizing agent described herein.

DETD In some aspects, the oxidation of the ***thiol*** ester occurs in the presence of a solvent. In some aspects, the solvent is water.

DETD The oxidizing agent that is contacted with the ***thiol*** ester can be any oxidizing agent capable of oxidizing a ***thiol*** group to a sulfonic acid group. In some embodiments, the oxidizing agent is oxygen. In other embodiments, the oxidizing agent is chlorine. In other embodiments, the oxidizing agent is dimethyl sulfoxide. In yet other embodiments, the oxidizing agent is a combination of a hydrogen halide and a catalytic amount of a dialkyl sulfide, such as dimethyl sulfoxide.

Other suitable oxidizing agents will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD The oxidation of the ***thiol*** ester can be performed at any temperature capable of converting the ***thiol*** ester to a sulfonic acid-containing ester. In some embodiments, the ***thiol*** ester is oxidized a temperature greater than -20.degree. C. In other embodiments, the ***thiol*** ester is oxidized at a temperature greater than 0.degree. C.; alternatively, greater than 20.degree. C.; or alternatively, greater than 50.degree. C.

DETD The time required for the oxidation of the ***thiol*** ester can be any time required to form the desired sulfonic acid-containing ester.

Generally, the time required for the oxidation of the ***thiol*** ester is at least 15 minutes; alternatively, at least 30 minutes; alternatively, at least 45 minutes; or alternatively, at least 1 hour.

In some embodiments, the time required for the oxidation of the ***thiol*** ester ranges from 15 minutes to 12 hours; alternatively, from 30 minutes to 6 hours; alternatively, from 45 minutes to 3 hours.

DETD The oxidation of the ***thiol*** ester can be performed at any pressure that maintains the ***thiol*** ester and the oxidation agent in the proper state, which is not always a liquid state, to

oxidize the ***thiol*** ester to a sulfonic acid-containing ester.

For example, when the oxidation agent is chlorine, the chlorine can be

in the gaseous state. In some embodiments, the oxidation of the ***thiol*** ester can be performed at a pressure ranging from 0 to 2000

psig. In other embodiments, the oxidation of the ***thiol*** ester

can be performed at a pressure ranging from 0 to 1000 psig; or alternatively, 0 to 500 psig.

DETD The oxidation of the ***thiol*** ester can be performed in a batch

reactor or a continuous reactor, as described herein.

Additionally, the process to produce the sulfonic acid-containing ester can comprise

additional process steps as recognized by those skilled in the art.

DETD The formation of the sulfonate-containing ester can be performed at any

temperature capable of converting the sulfonic acid group of the sulfonic acid-containing ester to a sulfonate group. In some embodiments, the sulfonate-containing ester is formed at a temperature

greater than -20.degree. C. In other embodiments, the

thiol

ester is oxidized at a temperature greater than 0.degree. C.; alternatively, greater than 20.degree. C.; or alternatively,

greater

than 50.degree. C. In yet other embodiments, the ***thiol*** ester

is oxidized at a temperature ranging from 0.degree. C. to 250.degree.

C.; alternatively, from 0.degree. C. to 150.degree. C.; or alternatively, from 20.degree. C. to 100.degree. C.

DETD A preferred sulfur-containing vegetable oil is MVO available from

Chevron Phillips Chemical Co. under the tradename Polymercaptopan 358.

Polymercaptopan 358 is made by the free radical addition of hydrogen

sulfide to the double bonds in soybean oil. Typically,

Polymercaptopan 358 has a ***thiol*** sulfur content of 5 to 10% and equivalent weights

of 640 to 320, respectively.

DETD Another preferred sulfur-containing vegetable oil useful as part of the

isocyanate-reactive component is a MHVO such as mercapto-hydroxy soybean oil. As described herein, a preferred mercapto-hydroxy soybean

oil is made by the free radical addition of hydrogen sulfide to epoxidized

soybean oil. Typically, the mercapto and hydroxy functionalities are

equal and the ***mercaptopan*** content is about 8.3%

thiol

sulfur. The equivalent weight of this material is 192, which

includes

both mercapto and hydroxy functionalities.
DETD Yet another preferred sulfur-containing vegetable oil useful as part of the isocyanate-reactive component is a CMVO such as sulfur cross-linked mercaptanized soybean oil. Sulfur cross-linked mercaptanized soybean oil is made by the addition of elemental sulfur to mercaptanized soybean oil. In this process, a portion of the ***mercaptan*** groups are consumed as cross-linking sites for the sulfur. Typical sulfur cross-linked mercaptanized soybean oil products by Chevron Phillips

Chemical Co. include Runs #22, 194, 195, 196 and 197 and have a ***thiol*** sulfur content ranging from about 8.0% to 1.4% and equivalent weights ranging from about 400 to about 2250, respectively.

DETD For epoxy polymer encapsulated CRF material made from sulfur-containing vegetable oil, it has been found that the use of a tertiary amine catalyst is highly preferred. The amount used is such to be sufficient to give the desired reaction rate for the production of the encapsulated slow release fertilizer product. A non-limiting example of a suitable amine catalyst is diazobicycloundecacene also known as 1,8-diazabicyclo[5.4.0]undec-7-ene [CAS# ***6674-22-2***] or "DBU", which is preferably used in the range of about 0.1% to 0.5% by weight of the coating. Other suitable catalyst materials will be apparent to those of ordinary skill in the art.

DETD The preferred sulfur-containing vegetable oil to be used in production of an epoxy polymer coated CRF material is MHVO such as mercapto-hydroxy

soybean oil. One such material is mercapto-hydroxy soybean oil known as

MHSO 566-84 produced by Chevron Phillips Chemical Co. This

preferred material contains 8.33% ***thiol*** sulfur, with an equivalent weight of 384, based upon the ***mercaptan*** functionality.

DETD The unsaturated ester used as a feedstock to produce the ***thiol*** ester compositions described herein can be described using a number of different methods. One method of describing the unsaturated ester feedstock is by the number of ester groups and the number of carbon-carbon double bonds that comprise each unsaturated ester oil

molecule. Suitable unsaturated ester used as a feedstock to produce the

thiol ester compositions described herein minimally comprise at

least 1 ester group and at least 1 carbon-carbon double bond. However, beyond this requirement, the number of ester groups and carbon-carbon double bonds comprising the unsaturated esters are independent elements and can be varied independently of each other. Thus, the unsaturated esters can have any combination of the number of ester groups and the number of carbon-carbon double bonds described separately herein. Suitable, unsaturated esters can also contain additional functional groups such as alcohol, aldehyde, ketone, epoxy, ether, aromatic groups, and combinations thereof. As an example, the unsaturated esters can also comprise hydroxy groups. An example of an unsaturated ester that contains hydroxy groups is castor oil. Other suitable unsaturated esters will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD In yet another aspect, the polyol or mixture of polyols used to produce the unsaturated ***thiol*** ester has a molecular weight or average molecular weight less than 500. In other embodiments, the polyol or mixture of polyols have a molecular weight or average molecular weight less than 300; alternatively less than 200; alternatively, less than 150; or alternatively, less than 100.

DETD Specific carboxylic acids used as a component of the carboxylic acid composition used to produce the unsaturated ester oil can have from 3 to 30 carbon atoms per carboxylic acid molecule. In some embodiments the carboxylic acid is linear. In some embodiments the carboxylic acid is branched. In some embodiments the carboxylic acid is a mixture of linear and branched carboxylic acids. In some embodiments the carboxylic acid can also comprise additional functional groups including alcohols, aldehydes, ketones, and ***epoxides***, among others.

DETD Minimally, the epoxidized unsaturated ester comprises at least one ***epoxide*** group. In an embodiment the epoxidized unsaturated ester comprises at least 2 ***epoxide*** groups; alternatively, at least 3 ***epoxide*** groups; or alternatively, at least 4 ***epoxide***.

In other embodiments, the epoxidized unsaturated ester comprises from 2 to 9 ***epoxide*** groups; alternatively, from 2 to 4

epoxide groups; alternatively, from 3 to 8 ***epoxide*** groups; or alternatively, from 4 to 8 ***epoxide*** groups. DETD In some embodiments, the unsaturated ester comprises a mixture of epoxidized unsaturated esters. In this aspect, the number of ***epoxide*** groups in the epoxidized unsaturated ester is best described as an average number of ***epoxide*** groups per epoxidized unsaturated ester molecule. In some embodiments, the epoxidized unsaturated esters have an average of at least 1.5 ***epoxide*** groups per epoxidized unsaturated ester molecule; alternatively, an average of at least 2 ***epoxide*** groups per epoxidized unsaturated ester molecule; or alternatively, an average of at least 2.5 ***epoxide*** groups per epoxidized unsaturated ester molecule; or alternatively, an average of at least 3 ***epoxide*** groups per epoxidized unsaturated ester molecule. In other embodiments, the epoxidized unsaturated esters have average of from 1.5 to 9 ***epoxide*** groups per epoxidized unsaturated ester molecule; alternatively, an average of from 3 to 8 ***epoxide*** groups per epoxidized unsaturated ester molecule; alternatively, an average of from 2 to 4 ***epoxide*** groups per epoxidized unsaturated ester molecule; or alternatively, from of 4 to 8 ***epoxide*** groups per epoxidized unsaturated ester molecule.

DETD The ***thiol*** composition can include an average of greater than 0 to about 4 ***epoxide*** groups per triglyceride. The ***thiol*** composition can also include an average of greater than 1.5 to about 9 ***epoxide*** groups per triglyceride.

DETD ***Mercaptans***

DETD Within some embodiments, an unsaturated ester or an epoxidized unsaturated ester is contacted with ***mercaptan***. Within these embodiments, the ***mercaptan*** can be any ***mercaptan*** comprising from 1 to 20 carbon atoms. Generally, the ***mercaptan*** can have the following structure: HS--R^{sup.3} wherein R³ is a C1 to C20 organyl groups or a C1 to C20 hydrocarbyl groups. In further embodiments the R³ can be a C2 to C10 organyl group or a C2 to C10 hydrocarbyl group. In some embodiments, the ***mercaptan*** composition comprises a solvent. In one aspect, the ***mercaptan*** composition comprises at least one other functional group.

DETD The at least one other functional group can be selected from several different groups. For example, the at least one other functional group

is an alcohol group, a carboxylic alcohol group, a carboxylic ester group, an amine group, a sulfide group, a ***thiol*** group, a methyl or ethyl ester of a carboxylic acid group, or combinations thereof. Other types of functional groups will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD In some embodiments, the ***mercaptan*** is selected from the group consisting of 3-mercaptopropyl-trimethoxysilane, 2-mercaptopypyridine, 4-mercaptopypyridine, 2-mercaptopypyrimidine, mercaptopyruvic acid, mercaptosuccinic acid, 2-mercaptopicotinic acid, 6-mercaptopicotinic acid, 2-mercaptophenol, 4-mercaptophenol, 3-mercpto-1,2-propanediol, 3-mercpto-1,2-propanediol, 3-mercaptopropanesulfonic acid, 1-mercaptopropanol, 3-mercaptopropanol, 2-mercaptopropionic acid, 3-mercaptopropionic acid, 2-mercaptopbenzyl alcohol, 3-mercaptop-2-butanol, 4-mercaptop-1-butanol, 2-mercaptopethanesulfonic acid, 2-mercaptopethanol, 2-mercaptopethyl ether, 2-mercaptopethyl sulfide, 16-mercaptopohexadecanoic acid, 6-mercpto-1-hexanol, 4'-mercaptopacetanilide, mercaptoacetic acid, 2-mercaptopbenzoic acid, 3-mercaptopbenzoic acid, 4-mercaptopbenzoic acid, 2-mercaptopthiazoline, 3-mercpto-1H-1,2,4-triazole, 11-mercaptopundecanoic acid, 1-mercpto-1-undecanol, or combinations thereof.

DETD In some embodiments, the ***mercaptan*** is selected from the group consisting of beta-mercaptopethanol, 2-mercaptophenol, 3-mercaptophenol, 4-mercaptophenol, 1-mercaptop-2-propanol, 1-mercaptop-3-propanol, mercaptoacetic acid, 2-mercaptopropionic acid, 3-mercaptopropionic acid, 2-mercaptopbenzoic acid, 3-mercaptopbenzoic acid, 4-mercaptopbenzoic acid, 2-mercaptopbenzylalcohol, 3-mercaptop-2-butanol, 4-mercaptop-1-butanol, 2-mercaptopethyl ether, 2-mercaptopethyl sulfide, 6-mercaptop-hexanol, 3-mercpto-1,2-propanediol, mercaptosuccinic acid, and mixtures thereof.

In further embodiments, the ***mercaptan*** is selected from the group consisting of beta-mercaptopethanol, 1-mercaptop-2-propanol, 1-mercaptop-3-propanol, 2-mercaptopbenzylalcohol, 3-mercaptop-2-butanol, 4-mercaptop-1-butanol, 6-mercaptop-hexanol, 3-mercpto-1,2-propanediol, and mixtures thereof. In further embodiments, the ***mercaptan*** is selected from the group consisting 2-mercaptophenol, 3-mercaptophenol, 4-mercaptophenol, and mixtures thereof. In yet further

embodiments, the ***mercaptan*** is selected from the group consisting of mercaptoacetic acid, 2-mercaptopropionic acid, 3-mercaptopropionic acid, 2-mercaptopbenzoic acid, 3-mercaptopbenzoic acid, 4-mercaptopbenzoic acid, mercaptosuccinic acid, and mixtures thereof.

DETD Within some embodiments, the inventive compositions described herein are reacted with an isocyanate compound to produce a polythiourethane composition. The isocyanate may be any isocyanates capable of reacting with the ***thiol*** esters, hydroxy ***thiol*** esters, and a cross-linked ***thiol*** esters described herein to form a polyurethane composition. Generally, the isocyanate compound has at least two isocyanate groups.

DETD In order to quantitatively measure the ***thiol*** sulfur, the ***thiol*** sulfur analyses were conducted using silver nitrate titration in accordance with ASTM D3227, with the following modifications designed to minimize probe fouling by silver salts: the silver samples were diluted in a known mass of tetrahydrofuran. The silver nitrate concentration was 0.01 N standardized against potassium iodide.

DETD ***Thiol*** sulfur was analyzed by three different tests. The first test used was the modified ASTM D3227, which resulted in a ***thiol*** sulfur measurement of 4.64%. The second test used to measure the ***thiol*** sulfur was SLP-1204, which is a test developed by Chevron Phillips Chemical Company LLP. By using the SLP-1204 test, the resulting ***thiol*** sulfur measurement was 4.28%. Lastly, the total sulfur was measured by combustion analysis, which resulted in a total sulfur measurement of 4.27%.

DETD Vegetable oil (42 kg) was charged to a 100-gallon holding vessel. The vessel was purged with nitrogen and returned to atmospheric pressure. Hydrogen sulfide (174 kg) was charged to the holding vessel. The vessel temperature was controlled from 25-30.degree. C. while the pressure was typically maintained between 380-400 psig. The reactants were continuously rolled from the holding tank through a stainless steel tubular photochemical reactor containing a 7.5 KW Hanovia medium pressure mercury lamp contained within a quartz tube. Reactor temperature, pressure, and composition were monitored over the course of the reaction. The reaction time was dependent upon reaching a desired

composition of ***thiol*** sulfur. Upon completion, the unreacted hydrogen sulfide was slowly vented from the system. Residual H.sub.2S was removed at 100.degree. C. and reduced pressure while passing nitrogen through a nitrogen sparge tube. The product was drained from the bottom of the reactor into a clean drum. The ***thiol*** sulfur measurements were 11.0% when using the modified ASTM D3227, 8.74% when using SLP-1204, and the total sulfur was 11.21% when using combustion analysis (total sulfur). DETD The resulting mercaptanized soybean oil was subjected to nitrogen sparging under reduced pressure at 100.degree. C. for a period of 4 hours to remove any residual hydrogen sulfide. The ***thiol*** sulfur measurements were 13.0% when using the modified ASTM D3227, 9.82% when using SLP-1204, and 11.69% when using combustion analysis. DETD Table 1 provides the properties of the mercaptanized soybean oil produced in examples 1-3.

TABLE 1

Mercaptanized Soybean Oil Product Properties			
C.dbd.C	Cyclic Sulfide to ***Thiol***		
	Thiol	Sulfur.sup..dagger. Group	
Example	to ***Thiol*** groups (wt %)	Molar Ratio	Molar Ratio
1	4.28	0.02	2.79
2	11.0	0.03	0.26
3	13.0	0.03	0.51

.sup..dagger. ***Thiol*** sulfur content determined by the modified ASTM D3227

DETD Soybean oil was charged to a 1000 gallon stirred reactor. Hydrogen sulfide was then charged to the reactor. After the hydrogen sulfide was charged to the reactor, the stirrers and the UV lamps were turned on and the reaction allowed to build temperature and pressure as the reaction proceeded. The reaction was continued until a minimum ***thiol*** sulfur content of 8 weight percent was achieved. After reaction was completion, the excess hydrogen sulfide was flashed from the reactor.

For runs 2-5, the mercaptanized soybean oil product underwent an additional hydrogen sulfide stripping step comprising stripping hydrogen sulfide from the product under vacuum, 50 mm Hg, at 250.degree. F. (only true for runs 2-5).

DETD Table 3 provides the details of the analysis of the mercaptanized soybean oil producing in the five 1000 gallon reactor runs.

TABLE 3

1000 gallon reactor Mercaptanized Soybean Oil Product Properties				
Run	Number	***Thiol*** Sulfur.sup..dagger. Group ***Thiol*** Groups	Cyclic Sulfide to Molar Ratio	Side Chain ***Thiol*** C.dbd.C groups
1	9.3	--	--	71.6
2	9.6	0.04	0.48	72.3
3	9.2	0.03	0.59	69.1
4	9.3	0.03	0.62	71.6
5	10.1	0.03	0.54	72.3

.sup..dagger. ***Thiol*** sulfur content determined by Raman spectroscopy

Mercaptanized Castor Bean Oil
DETD The analytical properties of the two mercaptanized castor oil products are provide in Table 4.

TABLE 4

Mercaptanized Castor Oil Product Properties				
Containing	***Thiol*** Sulfur.sup..dagger. Groups	***Thiol***	C.dbd.C to	Side Chain
Example	(wt %)	Molar Ratio	(%)	
1	6.4	0.52	64.1	
2	7.4	0.26	77.7	

.sup..dagger. ***Thiol*** sulfur content determined by Raman spectroscopy

Mercaptohydroxy Soybean Oil Synthetic Procedure
DETD Epoxidized Soybean Oil (700 g, about 0.7 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 4.7 g, 30.5 mmol) were charged to a 1-L Hastelloy C autoclave reactor that was pressure tested to 630 psig. Hydrogen sulfide (H₂S, 132.0 g, 3.87 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.degree. C. with stirring for 8 hrs, during which time the reactor pressure decreased from a maximum of 351 psig to 219 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H₂S was slowly vented to a low-pressure flare. The reactor vapor space

was then

swept with N₂ for 1 hr and the reactor contents drained warm (80-85° C.). The reaction product was N₂ sparged under

vacuum (<5 mmHg) at 130-140° C. for 16 hrs to remove residual

H₂S. The resulting light yellow, viscous sticky oil had a ***thiol*** sulfur (titration by modified ASTM D3227) content of 7.53

wt. %, 2.5 SH/molecule, or 2.35 meq SH/g. Combustion analysis indicated

C, 64.37%, H, 10.20%, N, <0.15%, and S, 9.51%. DEDT Epoxidized Soybean Oil (600 g, about 0.6 mol) and

1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged

to a 1-L Hastelloy C autoclave reactor, and the vessel was

pressure tested to 630 psig. Hydrogen sulfide (H₂S, 204.0 g, 5.99 mol) was

then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at

97° C. with stirring for 14 hrs, during which time the reactor pressure decreased from a maximum of 509 psig to 229 psig. The stirrer

was stopped and while still warm (90-95° C.), excess H₂S was

slowly vented to a low-pressure flare. The reactor vapor space was then

swept with N₂ for 1 hr and the reactor contents drained warm (80-85° C.). The reaction product was N₂ sparged under

vacuum (<5 mmHg) at 130-140° C. for 16 hrs to remove residual

H₂S. The resulting light yellow, viscous sticky oil had a ***thiol*** sulfur (titration by modified ASTM D3227) content of 4.14

wt. %, 1.4 SH/molecule, or 1.29 meq SH/g. Combustion analysis indicated

C, 65.18%, H, 10.17%, N, <0.15%, and S, 7.80%. DEDT Epoxidized Soybean Oil (600 g, about 0.6 mol) and

1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged

to a 1-L Hastelloy C autoclave reactor, and the vessel was

pressure tested to 630 psig. Hydrogen sulfide (H₂S, 204.0 g, 5.99 mol) was

then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at

85° C. with stirring for 10 hrs, during which time the reactor pressure decreased from a maximum of 578 psig to 489 psig. The stirrer

was stopped and while still warm (80-85° C.), excess H₂S was

slowly vented to a low-pressure flare. The reactor vapor space

was then

swept with N₂ for 1 hr and the reactor contents drained warm (80-85° C.). The reaction product was N₂ sparged under

vacuum (<50 mmHg) at 130-140° C. for 16 hrs to remove residual

H₂S. The resulting light yellow, viscous sticky oil had a ***thiol*** sulfur (titration with modified ASTM D3227) content of

8.28 wt. %, 2.8 SH/molecule, or 2.58 meq SH/g. Combustion analysis

indicated C, 65.24%, H, 9.52%, N, 0.18%, and S, 9.53%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged

to a 1-L Hastelloy C autoclave reactor that was pressure tested to 630

psig. Hydrogen sulfide (H₂S, 204.0 g, 5.99 mol) was then pressured

into the stirred reactor contents through a dip tube in the liquid

space. The reaction mixture was heated and maintained at 85° C.

with stirring for 12 hrs, during which time the reactor pressure decreased from a maximum of 587 psig to 498 psig. The stirrer was stopped and while still warm (80-85° C.), excess H₂S was

slowly vented to a low-pressure flare. The reactor vapor space was then

swept with N₂ for 1 hr and the reactor contents drained warm (80-85° C.). The reaction product was N₂ sparged under

vacuum (<50 mmHg) at 130-140° C. for 16 hrs to remove residual

H₂S. The resulting light yellow, viscous sticky oil had a ***thiol*** sulfur (titration with modified ASTM D3227) content of 8.24

wt. %, 2.8 SH/molecule, or 2.57 meq SH/g. Combustion analysis indicated

C, 63.39%, H, 10.01%, N, <0.15%, and S, 8.76%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged

to a 1-L Hastelloy C autoclave reactor, and the vessel was pressure

tested to 630 psig. Hydrogen sulfide (H₂S, 204.0 g, 5.99 mol) was

then pressured into the stirred reactor contents through a dip tube in

the liquid space. The reaction mixture was heated and maintained at

85° C. with stirring for 8 hrs, during which time the reactor

pressure decreased from a maximum of 606 psig to 537 psig. The stirrer

was stopped and while still warm (80-85° C.), excess H₂S was

slowly vented to a low-pressure flare. The reactor vapor space was then

swept with N₂ for 1 hr and the reactor contents drained warm

(80-85.degree. C.). The reaction product was N.sub.2 sparged under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove residual H.sub.2S. The resulting light yellow, viscous sticky oil had a ***thiol*** sulfur (titration by modified ASTM D3227) content of 7.34 wt. %, 2.5 SH/molecule, or 2.29 meq SH/g. Combustion analysis indicated C, 64.47%, H, 10.18%, N, <0.15%, and S, 8.40%. DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged to a 1-L Hastelloy C autoclave reactor that was pressure tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.degree. C. with stirring for 6 hrs, during which time the reactor pressure decreased from a maximum of 586 psig to 556 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H.sub.2S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove residual H.sub.2S. The resulting light yellow, viscous sticky oil had a ***thiol*** sulfur (titration by modified ASTM D3227) content of 5.93 wt. %, 2.0 SH/molecule, or 1.85 meq SH/g. Combustion analysis indicated C, 65.26%, H, 10.19%, N, <0.15%, and S, 8.43%. DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged to a 1-L Hastelloy C autoclave reactor, and the vessel was pressure tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.degree. C. with stirring for 4 hrs, during which time the reactor pressure decreased from a maximum of 595 psig to 554 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H.sub.2S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged under

vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove residual H₂S. The resulting light yellow, viscous sticky oil had a ***thiol*** sulfur (titration by modified ASTM D3227) content of 5.36 wt. %, 1.8 SH/molecule, or 1.67 meq SH/g. Combustion analysis indicated C, 65.67%, H, 10.17%, N, 0.34%, and S, 9.84%. DEDT Epoxidized soybean oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged to a 1-L Hastelloy C autoclave reactor that was pressure tested to 630 psig. Hydrogen sulfide (H₂S, 204.0 g, 5.99 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.degree. C. with stirring for 4 hrs, during which time the reactor pressure decreased from a maximum of 577 psig to 519 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H₂S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N₂ for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N₂ sparged under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove residual H₂S. The resulting light yellow, viscous sticky oil had a ***thiol*** sulfur (titration with AgNO₃) content of 5.85 wt. %, 2.0 SH/molecule, or 1.82 meq SH/g. Combustion analysis indicated C, 66.09%, H, 10.15%, N, 0.35%, and S, 10.63%. DEDT Epoxidized soybean oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged to a 1-L Hastelloy C autoclave reactor, and the vessel was pressure tested to 630 psig. Hydrogen sulfide (H₂S, 204.0 g, 5.99 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.degree. C. with stirring for 2 hrs, during which time the reactor pressure decreased from a maximum of 577 psig to 508 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H₂S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N₂ for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N₂ sparged under vacuum (<5 mmHg) at 130-140.degree. C. for 16 hrs to remove residual

H.sub.2S. The resulting light yellow, viscous sticky oil had a ***thiol*** sulfur (titration by modified ASTM D3227) content of 5.07 wt. %, 1.7 SH/molecule, or 1.58 meq SH/g. Combustion analysis indicated C, 63.96%, H, 10.01%, N, 0.35%, and S, 11.22%. DETD Table 5 provides the properties of the mercaptohydroxy soybean oil samples produced in Examples 1-10.

TABLE 5

per	***Mercaptan***				
	Epoxides		Sulfur	SH per	groups left
	Reaction	Reaction			
Example	Time (hrs)	Temp (.degree. C.)	(wt. %).sup.1	molecule.sup.2	
	molecule.sup.3	Molar Ratio			
1	0	N/A	N/A	0	4.3
--					
2	8	85	7.53	2.5	1.8
	0.72				
3	14	97	4.14	1.4	2.9
	2.07				
4	10	85	8.28	2.8	1.5
	0.54				
5	12	85	8.24	2.8	1.5
	0.54				
6	8	85	7.34	2.5	1.8
	0.72				
7	6	85	5.93	2.0	2.3
	1.15				
8	4	85	5.36	1.8	2.5
	1.40				
9	4	85	5.85	2.0	2.3
	1.15				
10	2	85	5.07	1.7	2.6
	1.529				

.sup.1Thiol sulfur was determined by silver nitrate oxidation using ASTM D 3227

.sup.2Determined by wt. % ***thiol*** sulfur

.sup.3Determined by subtracting the SH/molecule from the starting material

epoxide content

DETD Epoxidized soybean oil and the catalyst were charged to a 1-L Hastelloy

C autoclave reactor, and the vessel was pressure tested to 1000 psig.

Hydrogen sulfide was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated

and maintained at temperature a set period of time with stirring for 12

hrs. During the reaction time the reactor pressure usually decreased. At

the end of the reaction time, the stirrer was stopped and excess H_{sub.2}S was slowly vented while the reaction mixture was warm to a low-pressure flare. The reactor vapor space was then swept with N_{sub.2} for 1 hr and the reactor contents drained. The reaction product was N_{sub.2} sparged under vacuum (<50 mmHg) at 100.degree. C. for 16 hrs to remove residual H_{sub.2}S. Table 6 provides the reaction conditions used to produce the mercaptohydroxy soybean oils for several runs and the ***thiol*** sulfur content of the mercaptohydroxy soybean oils produced.

TABLE 6

Mercaptohydroxy Soybean Oil Production Runs

Run (minutes)	Epoxidized Soybean Oil (g) (wt. %)	Temperature (°C.)	Time (g)	H _{sub.2} S H _{sub.2} S:		***Epoxide*** Sulfur.sup.a (Molar Ratio (.degree. C.)
				Thiol (g)	Sulfur.sup.a Molar Ratio	
556-41.sup..dagger.	249.6 728		1.950	214.0	5.86	64
556-53.sup..dagger.	250.0 370		2.000	213.0	5.81	100
556-47.sup..dagger.	250.5 720		1.050	213.0	5.81	101
407-81D.sup..dagger.	500.0 480		4.200	255.0	3.49	85
407-86.sup..dagger.	600.0 600		5.000	204.0	2.07	85
556-79.sup..dagger-dbl.	250.0 720		2.600	214.0	5.83	100
556-80.sup..dagger-dbl.	251.0 720		5.000	214.0	5.81	100

.sup..dagger.Catalyst was DBU

.sup..dagger-dbl.catalyst was triethylamine (TEA)

.sup..atthiol sulfur measured by silver nitrate titration using modified ASTM D

3227

DETD Run number 407-86 was subjected to the sodium methoxide methanolysis

procedure and subsequently analyzed by GC/MS. The GS/MS analysis indicated that the product had ***epoxide*** group to ***thiol*** group molar ratio of approximately 0.14. The methanolysis data also

indicated that an average of 80.4 percent of the product mercaptohydroxy soybean oil contained sulfur.

DETD Mercaptonized soybean oil (900.1 g; 10.92 wt. % ***thiol*** sulfur,) was charged to a three necked flask along with elemental sulfur

pellets (9.6 g). The reaction mixture was heated to 120.degree. C. until sulfur dissolved and then cooled to 99.degree. C. Tributylamine (4.8 g) was charged to the reaction mixture with an addition funnel drop wise. The reaction mixture was mixed at 90.degree. C. for 2 hrs. H.sub.2S evolution was observed. The reaction product (904.8 g) was sparged with N.sub.2 under vacuum at 110.degree. C. for 4 hrs to remove residual H.sub.2S. The final product was a light yellow oil with a ***thiol*** sulfur of 6.33 wt. % (by modified ASTM D3227). The elemental combustion analysis was 70.19% C, 10.37% H; and 11.21% S.

DETD Mercaptanized soybean oil (900.0 g; 10.92 wt. % ***thiol*** sulfur,) was charged to a three necked flask along with elemental sulfur pellets (36.0 g). The reaction mixture was heated to 120.degree. C. until sulfur dissolved and then cooled to 100.degree. C. Tributylamine (4.8 g) was charged to the reaction mixture with an addition funnel drop wise. The reaction mixture was mixed at 90.degree. C. for 36 hrs. H.sub.2S evolution was observed. The reaction product (825.6 g) was sparged with N.sub.2 under vacuum at 90.degree. C. for 36 hrs to remove residual H.sub.2S. The reaction product was then sparged with N.sub.2 under vacuum at 110.degree. C. for 3 hrs to remove residual H.sub.2S. The final product was a light yellow oil with a ***thiol*** sulfur of 2.36 wt. % (by modified ASTM D3227). The elemental combustion analysis was 68.90% C; 11.07% H; and 12.25% S.

DETD Mercaptanized soybean oil (900.1 g; 10.92 wt. % ***thiol*** sulfur,) was charged to a three necked flask along with elemental sulfur pellets (18.0 g). The reaction mixture was heated to 125.degree. C. until sulfur dissolved and then cooled to 101.degree. C. Tributylamine (4.8 g) was charged to the reaction mixture with an addition funnel drop wise. The reaction mixture was mixed at 90.degree. C. for 2 hrs. H.sub.2S evolution was observed. The reaction product (901.5 g) was sparged with N.sub.2 under vacuum at 110.degree. C. for 4 hrs to remove residual H.sub.2S. The final product was a light yellow oil with a ***thiol*** sulfur of 4.9 wt. % (by modified ASTM D3227). The elemental combustion analysis was 69.58% C, 11.25% H; and 11.31% S.

DETD Mercaptanized soybean oil (900.2 g; 10.92 wt. % ***thiol*** sulfur,) was charged to a three necked flask along with elemental

sulfur pellets (45.0 g). The reaction mixture was heated to 125.degree. C. until sulfur dissolved and then cooled to 100.degree. C. Tributylamine (4.8 g) was charged to the reaction mixture with an addition funnel drop wise. The reaction mixture was mixed at 90.degree. C. for 2 hrs. H₂S evolution was observed. The reaction product (915.0 g) was sparged with N₂ under vacuum at 110.degree. C. for 4 hrs to remove residual H₂S. The final product was a light yellow oil with a ***thiol*** sulfur of 1.41 wt. % (by modified ASTM D3227). The elemental combustion analysis was 68.35% C, 10.98% H, and 13.28% S.

DETD Numerous polythiourethane compositions were prepared by reacting a ***thiol*** ester composition with a diisocyanate in the presence of a catalyst by using the processes described herein for preparing such polythiourethane compositions. The compositions were produced using the different variables of feedstocks, diisocyanates, stoichiometry, and catalysts shown in Table 8. Once every combination of variable was used, over 1200 compositions were produced. Each of the feedstocks were reacted with each of the diisocyanates at each of the stoichiometries with each of the catalysts listed to produce the 1200+ compositions. The stoichiometry was based upon a ***thiol*** ester composition (MSO, MHSO, CMSO, MCO) active hydrogen (***thiol*** and hydroxyl group) to diisocyanate equivalent ratio. For example, castor oil was reacted with toluene diisocyanate at a stoichiometric value of 1.25 while using Jeffol.RTM. A-480 as the catalyst. As another example, a ***thiol*** ester composition was reacted with methane diisocyanate at a stoichiometric value of 0.9 while using the DABCO catalyst.

DETD In the first MCO polythiourethane example, MCO was weighed into a polyethylene beaker. To the MCO agent was added Luprinate at a ***thiol*** to isocyanate mole ratio of 0.95. To this reaction mixture was added dibutyl tin dilaurate (DBTDL) at a weight percent of 0.125 based upon the total weight of the ingredients. The three-component reaction mixture was then manually stirred with a wooden Popsicle stick. The entire pre-polymer mixture was then poured into a mold for curing

and cured using curing profile B. After the curing time was complete it was determined that the preparation produced a polythiourethane polymer.

DETD In the second MCO polythiourethane example, MCO was weighed into a polyethylene beaker. To the MCO agent was added Luprinate M20S at a ***thiol*** to isocyanate mole ratio of 1.00. To this reaction mixture was added dibutyl tin dilaurate (DBTDL) at a weight percent of 0.125 based upon the total weight of the ingredients. The three-component reaction mixture was then manually stirred with a wooden Popsicle stick.

The entire pre-polymer mixture was then poured into a mold for curing and cured using curing profile B. After the curing time was complete it was determined that the preparation produced a polythiourethane polymer.

DETD In the polythiourethane compositions, the feedstock ***thiol*** ester compositions that were used included MSO (mercaptopanized soybean oil), MHSO (mercaptophydroxy soybean oil), CMSO (cross-linked mercaptopanized soybean oil), castor oil, and MCO (mercaptopanized caster oil). The diisocyanates that were used to produce these compositions included MDI (4,4'-methylenebis(phenyl) diisocyanate), HMDI (4,4'-methylenebis(cyclohexyl) diisocyanate, which is also known as hydrogenated MDI), TDI (tolylene 2,4-diisocyanate), HDI (1,6-diisocyanatohexane, which is also known as hexamethylene diisocyanate), and Luprinate.TM. M20S (which is an oligomerized form of MDI and is also referred to as polymeric MDI that is produced by BASF Corporation). The catalysts that were used included DABCO (diazabicyclooctane--di-tertiary amine), DBTDL (dibutyl tin dilaurate--organometallic catalyst), Jeffol.RTM. A-480 (which is a tertiary amine polyol produced by Huntsman Based Chemicals), and BDMA (benzyldimethylamine).

DETD In the Fertilizer Examples, the following materials were used:

A: Fertilizer particles--granular fertilizer grade urea, SGN 250, commercially available from Agrium;

B1: Mercaptopanized soybean oil (an example of MVO discussed above)--Polymercaptan 358, available from Chevron Phillips Chemical Co.;

8.65% ***thiol*** sulfur; 370 equivalent weight; viscosity of 510.6 cSt @ 21.degree. C.;

B2: Mercapto-hydroxy soybean oil (an example of MHVO discussed above)--A

mercapto-hydroxy soybean oil made by the free radical addition of hydrogen sulfide to epoxidized soybean oil; the mercapto and hydroxy functionalities are equal; 8.335% ***thiol*** sulfur, equivalent weight 192 (including both mercapto and hydroxy functionalities); B3: Sulfur cross-linked mercaptanized soybean oil (an example of CMVO discussed above)--A sulfur cross-linked mercaptanized soybean oil made by the addition of elemental sulfur to mercaptanized soybean oil; ***thiol*** sulfur content 6.33%; equivalent weight 506; B4: Sulfur cross-linked mercaptanized soybean oil (an example of CMVO discussed above)--A sulfur cross-linked mercaptanized soybean oil made by the addition of elemental sulfur to mercaptanized soybean oil; ***thiol*** sulfur content 7.64%; equivalent weight 419; cross-link/cross-link C1: Isocyanate #17--A polymeric MDI, commercially available from BASF Canada, equivalent weight of 133; C2: Epoxy resin--5 minute epoxy resin, commercially available from ITW Devcon, Danvers, Mass. 01923 USA, equivalent weight 198; D1: Organic additive--Gulfene C30-HA alpha olefin wax, commercially available from Chevron Phillips Chemical Co., melting point 65.degree. C.-80.degree. C.; D2: Organic additive--Calwax 170, a microcrystalline wax commercially available from Calwax Corporation; E: Cross-linking agent--Jeffol A480, commercially available from Huntsman Polyurethanes; equivalent weight of 120; functionality 4.0; viscosity of 4000 cPs @25C; F1: Amine catalyst: Exp-9, commercially available from Huntsman Polyurethanes; and F2: Amine catalyst: 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), CAS# ***6674-22-2*** .

DETD Analysis of the ***Thiol*** Containing Esters, Hydroxy ***Thiol*** Containing Esters and Cross-Linked ***Thiol*** Containing Ester

DETD Particular aspects of the ***thiol*** containing esters, hydroxy ***thiol*** containing esters, cross-linked ***thiol*** ester, unsaturated esters and epoxidized unsaturated esters are measured particular analytical techniques. ***Thiol*** sulfur values were obtained using a silver nitrate titration as described in ASTM D3227 or by Raman spectroscopy. Carbon-carbon double bond to ***thiol*** group molar ratio, cyclic sulfide to ***thiol*** group molar ratios were determined by .sup.13C NMR and/or GC analysis of the ***thiol*** containing ester or hydroxy ***thiol*** containing ester side chains.

DETD ***Thiol*** Sulfur Content by Raman Spectroscopy

DETD ***Thiol*** sulfur content was measured by both silver

nitrate titration, ASTM D3227, and/or Raman spectroscopy. The Raman spectroscopy method is practiced by measuring the Raman spectra of the ***thiol*** containing ester, hydroxy ***thiol*** containing ester, cross-linked ***thiol*** ester and comparing the spectra to calibration standards containing know ***thiol*** compounds having know amounts of ***thiol*** groups. Generally, the calibration standard ***thiol*** compound has a similar structure to the ***thiol*** containing esters analyzed.

DETD The ***thiol*** containing esters, hydroxy ***thiol*** containing esters and cross-linked ***thiol*** ester ***thiol*** content were determined by comparing the Raman spectra of the ***thiol*** containing esters, hydroxy ***thiol*** containing esters and cross-linked ***thiol*** ester to calibration standards prepared from mercaptanized methyl oleate diluted in soybean oil to known ***thiol*** sulfur contents. ***Thiol*** sulfur calibration standards were prepared using standards using various known concentration of mercaptanized methyl oleate diluted in soybean oil.

DETD Raman spectra of the calibration standards and the ***thiol*** containing esters, hydroxy ***thiol*** containing esters and cross-linked ***thiol*** ester were measured using a Kaiser Hololab 5000 Process Raman spectrometer, using a 785 nm laser.

Thiol containing esters, hydroxy ***thiol*** containing esters and cross-linked ***thiol*** ester samples and the ***thiol*** sulfur calibration standard Raman spectra were obtained by collecting four 10 second scans which were then processed using Holoreact software.

Thiol sulfur values for the ***thiol*** containing esters, hydroxy ***thiol*** containing esters and cross-linked ***thiol*** ester were then calculated using the ratio of the peak area values of the ***thiol*** SH peak (center: 2575 cm⁻¹; area 2500-2650 cm⁻¹), and the C.dbd.O peak (center--1745 cm⁻¹; area--1700-1800 cm⁻¹) and comparing them to the peak area values for the calibration standards and interpolating the containing esters, hydroxy ***thiol*** containing esters and cross-linked ***thiol*** ester ***thiol*** sulfur contents. Repeatability of the ***thiol*** sulfur values as measured

by Raman spectroscopy have been shown to have a standard deviation of 0.05-0.1 and a % RSD of 0.6-1.5 using 5 samples having a % ***thiol*** sulfur content ranging from 3.1-10.6 weight percent as measured over a two month period.

DETD The Raman spectroscopy technique for determining the ***thiol*** sulfur content of a ***thiol*** containing ester, hydroxy ***thiol*** containing ester, and a cross-linked ***thiol*** containing ester has been illustrated using a ***thiol*** containing ester produced from soybean oil. However, one skilled in the art may adapt and apply the Raman spectroscopy technique for determining the ***thiol*** sulfur content of other ***thiol*** containing esters, hydroxy ***thiol*** containing esters, and a cross-linked ***thiol*** containing esters described herein.

DETD C.dbd.C to ***Thiol*** Group and Cyclic Sulfide Group to Tool Group

Molar Ratios by .sup.13C NMR

DETD Carbon-carbon double bond to ***thiol*** group molar ratio and cyclic sulfide group to ***thiol*** group molar ratios were determined by .sup.13C NMR. ***Thiol*** containing ester .sup.13C NMR spectra were obtained on a Varian Mercury INOVA400 NMR, a Varian Mercury Plus 300 NMR, or equivalent spectrometer (75.5 MHz .sup.13C NMR). Peak areas were determined for the cyclic sulfide carbon atoms, ***thiol*** group HS--C carbon atoms and carbon-carbon double bonds carbon atoms using the .sup.13C NMR regions indicated in the table below:

Functional Group	.sup.13C NMR Region	Number of Carbon Atoms/Group
Cyclic Sulfide Carbon Atoms	49-49.5 ppm	2
HS--C Carbon Atoms	40-41.5 ppm	1
C.dbd.C Carbon Atoms	120-140 ppm	2
DETD The ***thiol*** containing ester cyclic sulfide to ***thiol*** group molar ratio were calculated by dividing the cyclic sulfide carbon atoms .sup.13C NMR peak area by 2 (to account for the 2 carbon atoms per cyclic sulfide group) and dividing the resultant number by the ***thiol*** group HS--C carbon atoms .sup.13C NMR peak area.		
The ***thiol*** containing ester carbon-carbon double bond to ***thiol*** group molar ratio were calculated by dividing the		

C.dbd.C

carbon atoms .sup.13C NMR peak area by 2 (to account for the 2 carbon atoms per carbon-carbon double bond) and dividing the result number by the ***thiol*** group HS--C carbon atoms .sup.13C NMR peak area. Offset sample .sup.13C NMR's for soybean oil and a ***thiol*** containing ester produced from soybean oil using the disclosed process

is provided as FIG. 1.

DETD The NMR technique for analyzing the unsaturated ester and the ***thiol*** containing ester produced from an unsaturated ester have been illustrated using .sup.13C NMR on soybean oil the ***thiol*** containing ester produced from soybean oil. However, one skilled in the art may adapt and apply either the .sup.13C NMR or .sup.1H NMR technique to analyze the unsaturated esters and ***thiol*** containing ester produced from the unsaturated ester described herein.

DETD ***Epoxide*** Group to ***Thiol*** Group Molar Ratios by .sup.13C or .sup.1H NMR

DETD The ***epoxide*** group to ***thiol*** group molar ratios were determined using .sup.1H or .sup.13C NMR. Hydroxy ***thiol*** containing ester .sup.1H or .sup.13C NMR spectra were obtained on a

Varian Mercury INOVA400 NMR, a Varian Mercury Plus 300 NMR, or equivalent spectrometer (300 MHz .sup.1H NMR-75.5 MHz .sup.13C NMR).

Peak areas were determined for the ***epoxide*** group and sulfide group using the .sup.13C and or .sup.1H regions indicated in the table below:

Functional Group	.sup.1H NMR Region	.sup.13C NMR Region	Number of Atoms/Group	Number of Atoms/Group
Epoxide Group	2.75-3.2 ppm	53.6-56.6 ppm	2	
2 Carbon Atoms				
HS--C Carbon Atoms	3.2-4 ppm	40-41.5 ppm	1	1
DETD group to	The hydroxy ***thiol*** containing ester ***epoxide***			
	thiol group molar ratio were calculated by dividing the ***epoxide*** group carbon atoms .sup.1H NMR peak area by 2			
(to group	account for the 2 hydrogen atoms attached to the ***epoxide*** carbon atoms) and dividing the result number by the ***thiol*** group HS--C carbon atom hydrogens 1C NMR peak area. Similarly, the			

hydroxy ***thiol*** containing ester ***epoxide*** group to ***thiol*** group molar ratio were calculated using ¹³H NMR peak areas.

DETD The average number of ***epoxide*** group per epoxidized unsaturated ester molecule can be determined utilizing similar methods utilizing either the carbonyl group carbon atom or the C--O ester group carbon atoms ¹³C NMR peak areas in conjunction with the ***epoxide*** group ¹³C NMR peak area. Sample ¹H NMR's epoxidized soybean oil and a ***thiol*** containing ester produced from epoxidized soybean oil 1 are provided in FIG. 2.

DETD The NMR technique for analyzing the epoxidized unsaturated ester and the ***thiol*** containing ester produced from an epoxidized unsaturated ester (a hydroxy ***thiol*** containing ester) has been illustrated using ¹H NMR on epoxidized soybean oil the ***thiol*** containing ester produced from epoxidized soybean oil. However, one skilled in the art may adapt and apply either the ¹H NMR or ¹³C NMR technique to analyze the epoxidized unsaturated esters and ***thiol*** containing ester produced from the epoxidized unsaturated ester described herein.

DETD Analysis of Unsaturated Esters, Epoxidized Unsaturated Esters, ***Thiol*** Containing Esters, and Hydroxy ***Thiol*** Containing Esters by Methanolysis

DETD Many properties of the unsaturated esters, epoxidized unsaturated esters, ***thiol*** containing esters, and hydroxy ***thiol*** containing ester were and/or can be determined by converting the complex ester molecules into their component polyols and carboxylic acid methyl esters. The converted esters are then analyzed by gas chromatography (GC) and/or gas chromatography/mass spectrometry (GCMS) to determine the composition of the complex ester side chains. Properties that are or can be determined by the methanolysis followed by GC or GC/MS of the carboxylic acid methyl esters include the number of side chain that contain ***thiol*** groups, the percent of ***thiol*** group sulfur, the number of (or average number) of double bonds per ester molecule, the molecular weight distribution (or average molecular weight) of the ester side chains, The number of (or average number of) ***epoxide*** groups per ester molecule, the cyclic sulfide

to ***thiol*** group molar ratio, the carbon-carbon double bond to ***thiol*** group molar ratio, and the ***epoxide*** group to ***thiol*** group molar ratio, among others.

DETD Depending upon the material being subjected to the methanolysis procedure, there are two methanolysis procedures that were practiced

 upon the unsaturated ester, epoxidized esters, ***thiol*** containing ester, and hydroxy ***thiol*** containing esters described within the experimental section.

DETD Unsaturated esters and ***thiol*** containing ester produced from

 unsaturated ester were subjected to a hydrogen chloride based methanolysis procedure. In the hydrogen chloride methanolysis procedure,

 a 50 to 100 mg sample of the ***thiol*** containing ester is contacted with 3 mL of 3 N methanolic HCl and reacted for 2 hours a

 50.degree. C. The solution is then allowed to cool and the neutralized

 with a dilute sodium bicarbonate solution. The solution's organic components are then extracted with ethyl ether and analyzed by GC and/or

 GC/MS. Additional details for the methanolic hydrogen chloride methanolysis procedure may be found in the product specification sheet

 for methanolic HCl, 0.5 N and 3 N as supplied by Supelco.

DETD Epoxidized unsaturated esters and hydroxy ***thiol*** containing esters produced from epoxidized unsaturated esters were subjected to a

 sodium methoxide based methanolysis procedure. The sodium methoxide

 methanolysis procedure was based upon the procedure disclosed in U.S.

 Pat. No. 3,991,089. In the sodium methoxide methanolysis procedure,

 approximately 1 g of the ester was placed in a 50 mL vial with 5.0 mL

 25% sodium methoxide in methanol, and 10 mL methanol. The mixture was

 shaken for approximately 1 hour at room temperature, during which time

 the solution became one phase. The mixture was then poured into 25 mL of

 distilled water. Diethyl ether, 25 mL, was added to the solution and the

 mixture was acidified with 0.5 N HCl to a pH of approximately 5. The

 organic layer was separated from the aqueous layer using a separatory funnel. The organic layer was washed successively with distilled water

 (15 mL) and brine solution (15 mL) and then dried over magnesium sulfate. The magnesium sulfate was separated from the organic solution

 by filtration and the solvent removed by rotary evaporation.

DETD FIG. 3 provides a GC/MS trace of a mercaptanized soybean oil

subjected

30 to the methanolysis procedure and analyzed by GC/MS using a HP-5
m.times.0.32 mm id.times.0.25 .mu.m film thickness GC Column.

Table 11

provides the GC/MS trace peak assignments.

TABLE 11

GC/MS Data for Methanolysis of A ***Thiol*** Containing Ester
Produced from
Soybean Oil
GC Retention time Methyl Ester Carboxylic Acid Assignment

21.58	Methyl hexadecanoate
23.66	Methyl (C18 monoene)oate
23.74	Methyl (C18 monoene)oate
23.96	Methyl octadecanoate
26.46	Methyl (C18 Monoene monomercaptan)oate
26.59	Methyl (C18 Monoene monomercaptan)oate
26.66	Methyl (C18 Monoene monomercaptan)oate
26.80	Methyl (C18 monomercaptan)oate
27.31	Methyl (C18 cyclic sulfide)oate
27.44	Methyl (C18 cyclic sulfide)oate
29.04	Methyl (C18 dimercaptan)oate
29.15	Methyl (C18 dimercaptan)oate
29.37	Methyl (C18 monoene dimercaptan)oate
29.46	Methyl (C18 monoene dimercaptan)oate
30.50	Methyl (C18 di (cyclic sulfide))oate

Peaks at 29.37 or 29.46 could also contain Methyl (C18 cyclic sulfide monomercaptan)oate isomers as part of those peaks.

DETD FIG. 5 provides a GC/MS trace of an epoxidized soybean oil contacted

with hydrogen sulfide (a hydroxy ***thiol*** containing ester) subjected to the methanolysis procedure and analyzed by GC/MS using a

HP-5 30 m.times.0.32 mm id.times.0.25 .mu.m film thickness GC Column.

Table 13 provides the GC/MS trace peak assignments.

TABLE 13

GC/MS Data for Methanolysis of a Hydroxy ***Thiol*** Containing Ester
Produced from Epoxidized Soybean Oil
GC

Retention

time

Methyl Ester Carboxylic Acid Assignment

16.09	Methyl hexadecanoate
17.68	Methyl octadecanoate
18.94	Methyl (C18 monoepoxide)oate
19.94	Methyl (C18 diepoxide)oate
20.14	Methyl (C18 diepoxide)oate
20.75	Methyl (C18 monohydroxy monothiol)oate
21-21.5	Methyl (C18 triepoxide)oate
22.82	Methyl (C18 dihydroxy dithiol)oate
22.90	Methyl (C18 monoepoxide monohydroxy monothiol)oate

27-27.5 Unidentified mixture of C18 sulfur containing methyl esters

DETD The methanolysis procedure and GC/MS procedure has been illustrate using soybean oil, epoxidized soybean oil, and the ***thiol*** containing products derived from soybean oil and epoxidized soybean oil.

However, one skilled in the art can easily adapt the procedures to the analysis of other unsaturated esters, epoxidized unsaturated ester, and the ***thiol*** containing products derived from the unsaturated esters and epoxidized unsaturated esters as described herein.

DETD The polythiourethane produced from the ***thiol*** containing esters, hydroxy ***thiol*** containing esters, and cross linked ***thiol*** containing ester were analyzed using ASTM E1545-95A and E228-95 to provide the glass transition temperatures and the coefficients of thermal expansion. Shore hardness of the polythiourethanes were determined using ASTM D2240-02A. The polythiourethane were also subject to a subjective analysis classifying the polythiourethanes as hard, flexible, rubbery, rigid, tough, brittle, and other characteristics.

CLM What is claimed is:

1. A cross-linked ***thiol*** ester composition comprising ***thiol*** ester oligomers having at least two ***thiol*** ester monomers connected by a polysulfide linkage having a structure --S.sub.Q--, wherein Q is greater than 1.

CLM What is claimed is:

2. The cross-linked ***thiol*** ester composition of claim 1, wherein the ***thiol*** ester oligomers have at least three ***thiol*** ester monomers connected by polysulfide linkages.

CLM What is claimed is:

3. The cross-linked ***thiol*** ester composition of claim 1, wherein the ***thiol*** ester oligomers have from 3 to 20 ***thiol*** ester monomers connected by polysulfide linkages.

CLM What is claimed is:

4. The cross-linked ***thiol*** ester composition of claim 1, wherein the crosslinked ***thiol*** ester composition comprises ***thiol*** ester monomers and ***thiol*** ester oligomers.

CLM What is claimed is:

5. The cross-linked ***thiol*** ester composition of claim 4, wherein the ***thiol*** ester monomers and ***thiol*** ester oligomers have a total ***thiol*** sulfur content from 0.5 to 8 weight percent.

CLM What is claimed is:
6. The cross-linked ***thiol*** ester composition of claim 4,
wherein the combined ***thiol*** ester monomers and
thiol
ester oligomers have an average molecular weight greater than
2000.

CLM What is claimed is:
7. The cross-linked ***thiol*** ester composition of claim 4,
wherein the ***thiol*** ester monomers and ***thiol***
ester
oligomers have an average molecular weight from 2000 to 20,000.

CLM What is claimed is:
8. The cross-linked ***thiol*** ester composition of claim 4,
wherein the ***thiol*** ester monomers and ***thiol***
ester
oligomers have a total sulfur content ranging from 8 to 15 weight
percent.

CLM What is claimed is:
9. A cross-linked ***thiol*** ester composition produced by
the
process comprising the steps of: a) contacting a ***thiol***
ester
composition with an oxidizing agent; and b) reacting the
thiol
ester and the oxidizing agent to form ***thiol*** ester
oligomers
having at least two ***thiol*** ester monomers connected by a
polysulfide linkage having a structure --S._{sub}.Q--, wherein Q is
greater
than 1.

CLM What is claimed is:
10. A process to produce a cross-linked ***thiol*** ester
composition comprising: a) contacting a ***thiol*** ester
composition with an oxidizing agent; and b) reacting the
thiol
ester and the oxidizing agent to form ***thiol*** ester
oligomers
having at least two ***thiol*** ester monomers connected by a
polysulfide linkage having a structure --S._{sub}.Q--, wherein Q is
greater
than 1.

CLM What is claimed is:
13. The process of claim 10, wherein the ***thiol*** ester is
a
hydroxy ***thiol*** ester.

CLM What is claimed is:
14. The process of claim 10, wherein a weight ratio of elemental
sulfur
to ***thiol*** sulfur in the ***thiol*** ester molecules
ranges
from 0.5 to 32.

CLM What is claimed is:
15. The process of claim 10, wherein step of the reacting the

thiol ester and the oxidizing agent is performed at a temperature ranging from 25.degree. C. to 150.degree. C.

CLM What is claimed is:
16. The process of claim 10, wherein residual hydrogen sulfide is stripped from the cross-linked ***thiol*** ester composition produced.

CLM What is claimed is:
17. The process of claim 12, wherein the reaction of the ***thiol*** ester and the elemental sulfur is catalyzed.

IT 102-85-2, Tri-n-butylphosphite ***6674-22-2*** ,
1,8-Diazabicyclo[5.4.0]undec-7-ene
(activator; thiol ester compns. prep'd. by reacting H2S with unsatd.

esters, such as soybean oil for manuf. monomers for prodn. of polythiocurethanes for fertilizers)

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